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This report describes the present status of our effort to develop and implement semi-empirical and theoretical methods for obtaining potential curves of diatomic excimer systems. A configuration inter-action calculation on GaKr is presented along with preliminary results of a Gordon-Kim calculation. The basic theory of the semi-empirical electron scattering model is also given.

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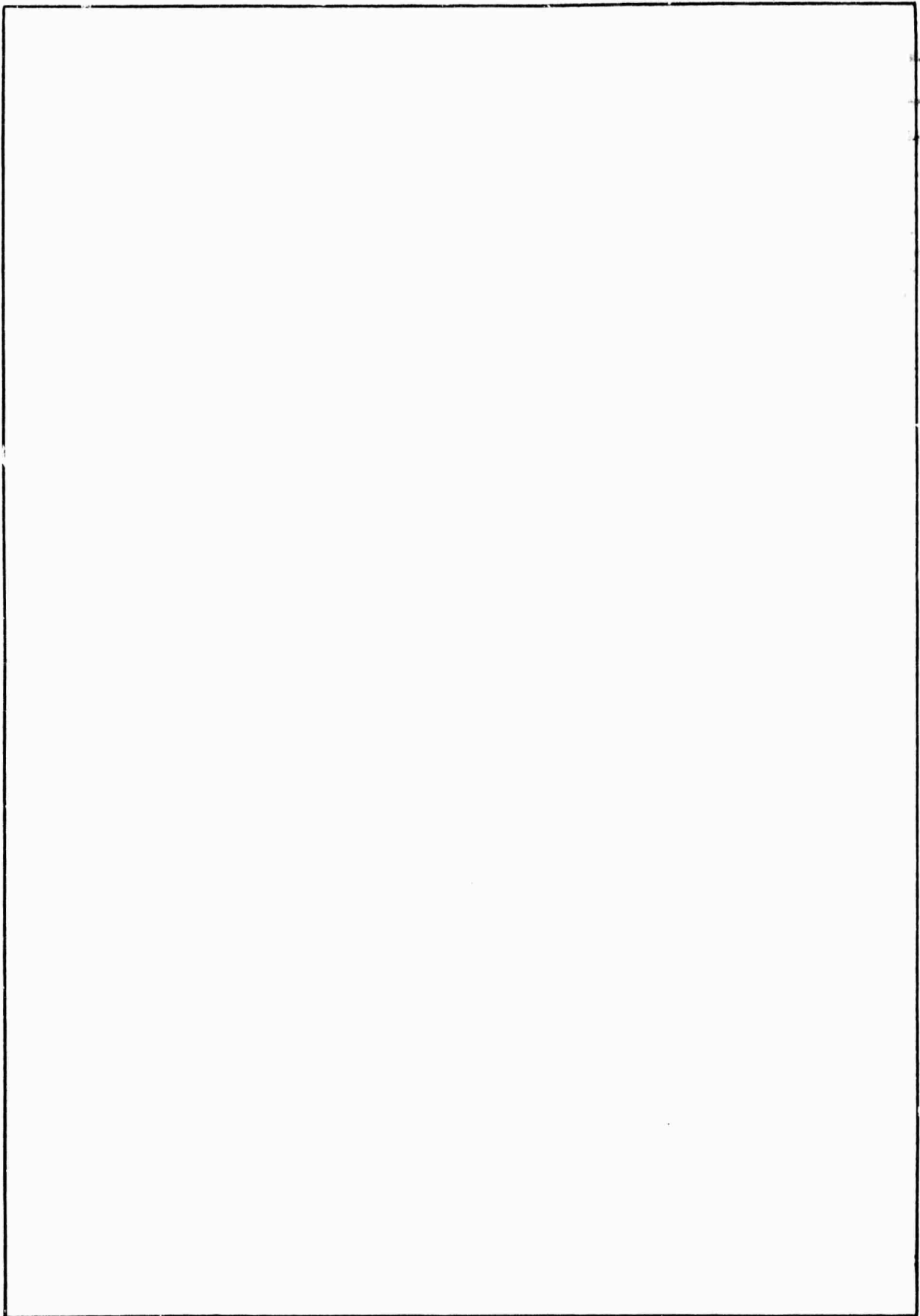
Annual Report # 1

October 1, 1976 - December 31, 1977

EXCIMER POTENTIAL CURVES

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I. Introduction

This Annual Scientific Report covers work performed under
Contract No. N00014-77-C-0102, entitled Excimer Potential Curves. This
report describes the present status of our effort to develop and implement
semi-empirical and theoretical methods for obtaining potential curves of
diatomic excimer systems. Our emphasis is on developing and testing
methods which will be reasonably accurate yet will not require long lead
times for development and will not require excessive amounts of computer
time for production runs. The object is to enable experimentalists to
choose or reject possible laser systems on the basis of inexpensive
theoretical calculations rather than on the basis of expensive and time-
consuming experiments.

We are particularly interested in developing methods that are applicable
to excimer systems because of the current emphasis on these systems as
candidates for efficient, high-power visible and ultraviolet lasers.
After consultation with A. V. Phelps and A. Gallagher of J.I.L.A., we
have decided to concentrate initially on molecules of rare gases with
Thallium, Indium or Gallium.

For systems with a large number of electrons, such as Tl-R , present
Configuration Interaction (CI) programs are inadequate and offer no hope
of extension in the immediate future. Consequently, our effort is con-
centrated on developing and testing semi-empirical methods that can easily
and rapidly be applied to the excimer systems of interest. This report

covers our progress in three areas: 1) We have performed a configuration interaction calculation on GaKr , 2) We are applying the Gordon-Kim theory to the group IIIB-rare gas systems, 3) We are continuing the development of the semi-empirical electron scattering model.

Our work in the first area is close to completion. The CI calculation on GaKr was done so that we can compare the results of our approximate methods with accurate potential curves. GaKr was chosen as the test system since it is the largest of the systems we are interested in for which a CI calculation can be done. The GaKr curves have been extrapolated to give curves for InKr and TlKr ; however, these extrapolation are very approximate. In particular, the positions and depths of the potential wells for InKr and TlKr are not given accurately. These potential curves have been used to predict the spontaneous emission and absorption coefficients for GaKr , InKr and TlKr . The details of this work are given in Section II, which is a rough draft of a paper on this work that will be submitted for publication.

Although at the time the proposal was written, applications of the Gordon-Kim electron gas theory to open shell systems had failed to give reasonable results, recent applications of the G-K theory to open shell - closed shell interactions have been successful (M. J. Clugston and R. G. Gordon, JCP 66, 239 (1977)). Consequently, we are now investigating the possibility of using this method to obtain approximate potential curves for GaR . Our preliminary calculations on GaKr are described in Section III.

The basic theory and computational method for the electron scattering model are described in Section IV. We are proceeding with this approach, in addition to the Gordon-Kim theory, because the electron-scattering model should provide a more accurate description of atomic distortion and should be applicable to a wider range of molecules than the G-K theory.

II. Electronic States of GaKr : <u>Ab initio</u> calculations of a prototype
     for TlKr

     The work in this section was performed in conjunction with Thom H.
Dunning, Jr. of Los Alamos Scientific Laboratory and is a rough draft of
a paper that will be submitted for publication.

Electronic States of GaKr : _Ab_ _initio_ calculations of a prototype for TlKr

I. Introduction

Among the metal-rare gas eximers, the TlXe system is believed to be an excellent candidate for an efficient visible, high power, tunable laser.[1] Since _ab_ _initio_ calculations on this system are beyond the scope of present computer programs, we present here a configuration interaction (CI) calculation on GaKr , which is the largest group IIIB-rare gas system for which CI calculations can be done. We use the calculated GaKr curves to model the potential curves for InKr and TlKr . Although our model does not allow further extrapolation from TlKr to TlXe , it is hoped that these calculations will yield some insight into the properties of the TlXe eximer. In addition, Gallagher[2] has recently raised the possibility of using GaXe as a laser if the Ga can be obtained from dissociation of GaI_3 . Consequently the GaKr curves should also be of intrinsic interest.

In this paper, the CI calculations on GaKr are presented along with the model calculations on InKr and TlKr . These potential curves are used as the basis of a classical calculation of the emission and absorption coefficients for these systems.

II. Details of the calculation

A. Basis set

The calculations use (14s11p6d) primitive Gaussian bases for gallium and krypton[3] as a starting point. The core orbitals (1s,2s,2p,3s,3p) are singly contracted to the Hartree-Fock atomic orbitals while the valence orbitals (4s and 4p) and the 3d orbitals are each described by two contracted functions(see Table I). The resulting (5s4p2d/5s4p2d) contracted bases are constructed using the general contraction scheme of Raffenetti.[4]

These basis sets are extended to include polarisation by adding two diffuse s functions (5s and 5s') and a diffuse p function (5p) to describe the lowest Rydburg orbitals. The exponents for these orbitals $(\zeta(5s) = .026, \zeta(5s') = .011, \zeta(5p) = .01)$ are obtained from atomic calculations on the excited states of Ga . The final basis set thus consists of a (16s12p6d) primitive basis contracted to [7s5p2d] for Ga and a (14s11p6d) primitive basis contracted to [5s4p2d] for Kr .

B. SCF calculation

The starting point for the CI calculation is a Hartree-Fock calculation on the $^2\Sigma^+$ state

$$. . . . . 13\sigma^2 14\sigma^2 7\pi^4 15\sigma^2 16\sigma .$$

The inner core molecular orbitals (twelve σ, twelve π and four δ) are held doubly occupied from this point on and are replaced by the rigorous nonlocal Hartree-Fock potential.

$$V_{core} = V_N + \sum_{i=core} (2J_i - K_i)$$

With the core orbitals removed from consideration, it is convenient to renumber the valence orbitals so that the Hartree-Fock configuration is written as

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma 1\pi^4$$

At large R the correspondence for the valence orbitals is

$1\sigma \rightarrow 4sKr$

$2\sigma \rightarrow 4pKr$

$3\sigma \rightarrow 4sGa$

$4\sigma \rightarrow 4pGa$

$1\pi \rightarrow 4pKr$

In addition to the valence orbitals, nine σ , six π and four δ virtual orbitals are used in the CI calculations. The lowest virtual orbitals (5σ, 6σ, 7σ, 2π, 3π), which correspond to the Ga 5s, 5s', 4p and 5p atomic orbitals for large internuclear separations, are obtained by the improved virtual orbital (IVO) procedure.[5] The IVO orbitals are obtained by removing the electron from the 4σ (valence) orbital of the above configuration and calculating the virtual orbitals for the (N-1)-electron Hamiltonian.

C.   CI calculations

Full polarization CI (POL-CI) calculations[6] which provide a balanced description of all states of the 4s-4p manifold were carried out. A set of reference configurations was chosen (see Table II) to describe the dominant configurations for the $^2\Sigma^+$ and $^2\Pi$ states of the molecule and the $^1\Sigma^+$ state of the ion.

The full POL-CI calculations include all (1+2) electron excitations relative to each reference configuration subject to the restrictions that no more than one electron occupy the Rydberg 5σ orbital and no more than one electron occupy any virtual orbital (6σ, 2π etc.). This results in 764 spatial and 2314 spin configurations for the $^2\Sigma^+$ states, 556 spatial and 1565 spin configurations for the $^2\Pi$ states and 368 spatial and 558 spin configurations for the $^1\Sigma$ state. A total of 15σ , 14π and 2δ occupied and virtual orbitals are used in the POL-CI calculations.

III. Results for GaKr

A. Electronic states without spin-orbit coupling

The interaction of ground state Ga (^{2}S) and Kr (^{1}S) atoms gives rise to a $^2\Pi$ and a $^2\Sigma^+$ state as shown schematically in Fig. 1. In the $^2\Sigma^+$ state the occupied 4p Ga orbital is oriented along the molecular axis while in the $^2\Pi$ state it is perpendicular to the axis. The $^2\Sigma^+$ state should be essentially repulsive inside the van der Waals region because of the unfavorable interaction of the $4p\sigma$ orbitals on Ga and Kr   The $^2\Pi$ state does not have this repulsive interaction so it should be more attractive. The interaction of excited Ga*(^{2}S) and ionic Ga$^+$(^{1}S) atoms with ground state Kr gives rise to a $^2\Sigma^+$ and a $^1\Sigma^+$ state respectively. In both cases these states are expected to be somewhat attractive.

The potential energy curves (Fig. 2 and Table III) from the POL-CI calculations generally follow the behavior predicted from these theoretical considerations. These calculations are not, however, designed to treat long-range dispersion forces. Many excitations which contribute to a $C_6 r^{-6}$ attraction are not included in the wavefunction. For these reasons, one would expect deeper wells in all the potential curves including the two lowest, generally repulsive, states. As predicted, the $1^2\Pi$ state is less repulsive than the $1^2\Sigma^+$ state. The bound excited state $2^2\Sigma^+$ has a minima at 6.36 a.u. about 3.0 eV above the ground state curve, while the minima in the ion curve is at 6.28 a.u. and 5.6 eV above the ground state. The well depths are compared with those obtained by Gallagher[11] in Table IV, and as expected, Gallagher's wells are deeper.

The dipole moments of these states and the transition moments between $^2\Sigma^+$ and the lower states have also been calculated and are given in Table V and Figs. 3 and 4.

B   Electronic states including spin-orbit coupling

A complete treatment of the electronic states of GaKr must include
the effects of spin-orbit coupling. The states considered here, which
dissociate to the closed-shell ground state of Kr and an open-shell state
of Ga or Ga^+ are influenced only by the spin-orbit matrix elements of
the open-shell atom.

Following the procedure used previously,[7,8,9,10] we have adopted a
simple model for including the effects of spin-orbit coupling on the
calculated potential energy curves and wavefunctions. The experimental
spin-orbit parameters for the open-shell atom (Ga and later In , Tl) are
used to determine the matrix elements of the spin-orbit interaction, H_{so} ,
coupling the molecular states at infinite separation and these matrix
elements are assumed to be independent of internuclear distance. The
resulting spin-orbit matrix H_{so} is added to the diagonal matrix of
electronic energies $H_{elec}(R) = \delta_{ij}E_i(R)$:

$$H(R) = H_{elec}(R) + H_{so}$$

and the total matrix H is then diagonalized at each internuclear distance
R . Thus, in addition to the assumption that the spin-orbit matrix elements
do not change as functions of R , this model assumes that only one-center
terms need be included so that only the spin-orbit coupling on Ga is
important. We would expect this procedure to provide reasonable results
to the extent that the molecular states retain the identity of the atomic

states from which they are formed. The spin-orbit matrices are given in Table VI along with the atomic parameters used in these calculations. The parameter λ is chosen so that the atomic $^2P_{3/2}$ and $^2P_{1/2}$ states have energies of $+\lambda$ and -2λ respectively.

We shall label the molecular states using the convention of Hund's case (c) where Ω , the projection of total angular momentum along the molecular axis, is the only good quantum number. Ω is defined as $\Omega = \Lambda + S_z$, where Λ and S_z are the orbital and spin angular momentum projection, respectively. The molecular $^2\Sigma^+$ states have only a $\Omega = 1/2$ component, while the $^2\Pi$ states yield a $\Omega = 3/2$ and $\Omega = 1/2$ state. The states in the Ω representation are labeled according to increasing energy by a Roman numeral. So the $\Omega = 1/2$ states are designated as I 1/2 , II 1/2 and the $\Omega = 3/2$ states are I 3/2 , II 3/2 .

The coupled states are expressed as follows:

$$|I\ 1/2 > = C_\Sigma |1^2\Sigma^+> + C_\Pi |1^2\Pi>$$
$$|II\ 1/2 > = -C_\Pi |1^2\Sigma^+> + C_\Sigma |1^2\Pi>$$
$$|I\ 3/2 > = |1^2\Pi>$$

The spin-orbit coefficient C_Σ and C_Π are given in Table VII. The potential curves and transition moments for GaKr including spin-orbit coupling are given in Table VIII and Figs. 5 and 6.

IV. Extrapolations to InKr and TlKr

The potential curves for InKr and TlKr are modeled on the
GaKr curves. The lowest excitation energies and the ionization potentials
for the series Ga , In , Tl are given in Table IX. As can be seen, this
series does not form a steady progression. In has a lower ionization
potential and lower excitation energies than Ga , as expected for a
heavier atom. However, Tl has a higher ionization potential and higher
excitation energies. This is due in part to the presence of a filled
4f shell in Tl and the larger spin-orbit effects.[12] These effects
should be considered when extrapolating the GaKr curves to InKr and
TlKr.

To simulate InKr and TlKr , the experimental spin-orbit parameters
for In and Tl are used to couple the GaKr curves. The curves are
also shifted to give the correct atomic excitation energies at $R = \infty$
(see Table IX). This procedure should give at best a qualitative description
of states of InKr and TlKr , since the non-spin-orbit coupled states
are expected to have quantitatively different well depths and equilibrium
separations.

The effect of the increasing spin-orbit perturbation in going from
Ga to In and Tl is evident in the calculated curves which are given
in Figs. 7 and 8. Only the well depths and positions for the I 1/2 and
II 1/2 states are affected by the spin-orbit coupling. The other states

are the same as those for GaKr except that they have the correct
asymptotic spacing.

The mixing parameters from the spin-orbit coupling calculations for
TlKr are also used as the coefficients of the GaKr wave function to
estimate the transition moments for this system. The TlKr transition
moments are given in Table X and Fig. 9.

V. Absorption and stimulated emission coefficients for possible laser transitions

The interest in the group IIIB-rare gas systems arises from the possibility of their use as visible laser systems. In order to judge their usefulness as lasers it is convenient to calculate the absorption $k_\nu(t)$ and stimulated emission $g_\nu(T)$ coefficients. Obtaining quantum-mechanical results for these quantities would require a complex calculation which would be inconsistent with the extrapolations used to obtain the InKr and TlKr curves. Consequently, we have used Gallagher's analysis [17], which is based on the classical Frank-Condon principle.

In order to obtain g_ν and k_ν, the CI curves are first fit by Morse potentials. The parameters for these Morse potentials are given in Table XI. These parameters can then be used in Gallagher's equations, along with the atomic transition rate, to obtain absorption and stimulated emission coefficients for pressure and excitation conditions of interest to experimentalists. We have calculated these coefficients for two different types of conditions. The high temperature results correspond to the case where the concentration of the metal is obtained from the vapor pressure of the metal itself, while the low temperature results correspond to obtaining the required concentration of the metal from vaporization of MI_3 (M = Ga, In, or Tl). This latter condition has been suggested by Gallagher as a possible means of obtaining high concentrations of the metal at low temperatures. In both cases the densities used are $10^{20}/cm^3$ for Kr, $10^{16}/cm^3 = 3[M\ ^2P_{1/2}] = 1.5[M\ ^2P_{3/2}]$ and $2 \times 10^{14}/cm^3 = [M\ ^2S_{1/2}]$. The resulting absorption and stimulated

emission coefficients for GaKr , InKr and TlKr are given in Figures 10 to 15.

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Table I. Gaussian exponents and contraction coefficients

Exponents	Contraction coefficients				

Gallium atom

	1s	2s	3s	4s	4s'
457600.	.000222	-.000069	.000026	-.000006	0.0
68470.	.001732	-.000535	.000205	-.000048	0.0
15590.	.008952	-.002814	.001070	-.000247	0.0
4450.	.035874	-.011275	.004337	-.001007	0.0
1472.	.114000	-.038495	.014707	-.003399	0.0
541.3	.274138	-.100714	.039748	-.009279	0.0
214.8	.414793	-.211832	.084475	-.019587	0.0
88.81	.275395	-.175448	.079654	-.019104	0.0
27.18	.029561	.479840	-.291821	.072753	0.0
11.54	-.006815	.634145	-.527118	.134137	0.0
3.303	.002253	.069592	.583707	-.181778	0.0
1.334	-.001017	-.012299	.674103	-.358241	0.0
.1947	.000251	.002774	.028077	.615164	0.0
.07158	0.0	0.0	0.0	0.0	1.0

	5s	5s'
.026	1.0	0.0
.011	0.0	1.0

	2p	3p	4p	4p'	5p
3274.	.001513	-.000576	.000094	0.0	0.0
765.4	.013070	-.004981	.000800	0.0	0.0
241.6	.067263	-.026421	.004337	0.0	0.0
89.39	.219542	-.089529	.014443	0.0	0.0
36.36	.421107	-.186734	.031377	0.0	0.0
15.60	.376515	-.144494	.021501	0.0	0.0
6.472	.089425	.258956	-.046233	0.0	0.0
2.748	-.000502	.570187	-.125293	0.0	0.0
1.090	.001761	.325305	-.045636	0.0	0.0
.2202	-.000247	.016563	.452811	0.0	0.0
.06130	0.0	0.0	0.0	1.0	0.0
.01	0.0	0.0	0.0	0.0	1.0

	3d	4d
59.66	.031949	0.0
17.10	.163546	0.0
6.030	.367457	0.0
2.171	.456851	0.0
.6844	.305161	0.0
.160	0.0	1.0

Table I. Gaussian exponents and contraction coefficients

Exponents	Contraction coefficients				
	Krypton atom				
	1s	2s	3s	4s	4s'
605700.	.000231	-.000073	.000029	-.000009	0.0
90300.	.001755	-.000551	.000221	-.000070	0.0
20920.	.009076	-.002894	.001159	-.000369	0.0
5889.	.036990	-.011834	.004781	-.001522	0.0
1950.	.116154	-.039826	.016056	-.005118	0.0
718.2	.278401	-.104801	.043454	-.013886	0.0
285.4	.415746	-.217093	.091899	-.029537	0.0
118.6	.267204	-.175562	.083789	.027309	0.0
38.16	.027870	.471395	-.303023	.103498	0.0
16.45	-.005998	.636794	-.570620	.208810	0.0
5.211	.002217	.082255	.501751	-.235737	0.0
2.291	-.001092	-.014138	.760483	-.553570	C.0
.4837	.000306	.003289	.044857	.701123	0.0
.1855	0.0	0.0	0.0	0.0	1.0

	2p	3p	4p	4p'	
4678.	.001392	-.000569	.000156	0.0	
1120.	.011666	-.004777	.001286	0.0	
357.1	.060858	-.025631	.007059	0.0	
131.4	.210040	-.092159	.024990	0.0	
52.86	.421000	-.200936	.056870	0.0	
22.70	.383515	-.160784	.040225	0.0	
9.547	.097383	.267789	-.084756	0.0	
4.167	-.001087	.585908	-.240291	0.0	
1.811	.002209	.291397	-.038636	0.0	
.5337	-.000509	.015484	.599154	0.0	
.1654	0.0	0.0	0.0	1.0	

	3d	4d			
125.6	.019168	0.0			
33.31	.125638	0.0			
12.15	.366069	0.0			
4.350	.502482	0.0			
1.494	.264377	0.0			
.35	0.0	1.0			

Table II. Reference Configurations

$^2\Sigma^+$ states

1 $\quad 1\sigma^2 2\sigma^2 3\sigma^2 4\sigma 1\pi^4$

2 $\quad 1\sigma^2 2\sigma^2 3\sigma^2 5\sigma 1\pi^4$

3 $\quad 1\sigma^2 2\sigma^2 3\sigma^2 6\sigma 1\pi^4$

$^2\Pi$ states

1 $\quad 1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 2\pi$

2 $\quad 1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 3\pi$

$^1\Sigma^+$ state (GaKr$^+$)

1 $\quad 1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4$

Table III. POL-CI calculations on the low-lying states of GaKr and the ground state of GaKr$^+$. All energies are relative to -4674. hartrees.

R	$1\,{}^2\Sigma^+$	$2\,{}^2\Sigma^+$	$1\,{}^2\Pi$	$1\,{}^1\Sigma^+$
∞	-1.200042	-1.095050	-1.198917	-0.992860
15.00	-1.200121	-1.095025	-1.198978	-0.993044
10.00	-1.200290	-1.094061	-1.199328	-0.994018
8.00	-1.198650	-1.094202	-1.200204	-0.996703
7.00	-1.193963	-1.095454	-1.200450	-0.999505
6.00	-1.179381	-1.096768	-1.197718	-1.002018
5.00	-1.135164	-1.088552	-1.179245	-0.992868
4.50	-1.086883	-1.064404	-1.148099	-0.967583
4.00	-1.018697	-0.992381	-1.079327	-0.906827
3.75	-0.968656	-0.933786	-1.025394	-0.856247

Table IV. Potential well depths

Mole-cule	State	CI		Morse Fit		Gallagher	
		R	ΔE(eV)	R	ΔE(eV)	R	ΔE(eV)
GaKr	$I_{1/2}(X_{1/2})$		$\sim$.018	7.55	.021		
	$I_{3/2}(X_{3/2})$		$\sim$.040	7.18	.040		
	$II_{1/2}(A_{1/2})$	$\sim$10	.006	10.15	.00642		
	$III_{1/2}(B^2\Sigma_{1/2})$	6.36	.064	6.26	.080		
GaKr$^+$	I_0	6.28	.26	5.95	.252		
InKr	$I_{1/2}$	$\sim$8	$\sim$.013	7.86	.00778		
	$I_{3/2}^a$						
	$II_{1/2}$	$\sim$10	$\sim$.006	9.98	.0064		
	$III_{1/2}^a$						
	I_0^a						
TlKr	$I_{1/2}$	$\sim$8	$\sim$.010	8.5	.012	7.01	.024
	$I_{3/2}^a$					6.58	.062
	$II_{1/2}$	$\sim$10	$\sim$.006	9.88	.064		
	$III_{1/2}^a$					6.09	.107
	I_0^a						

[a]same as GaKr

Table V. Dipole and transition moments for the low-lying states of GaKr

R	$X^2\Pi$	$1^2\Sigma^+$	$2^2\Sigma^+$	$1^2\Sigma^+-X^2\Pi$	$2^2\Sigma^+-X^2\Pi$	$2^2\Sigma^+-1^2\Sigma^+$
15.00	0.00598	0.00156	0.07558	0.00183	-1.29167	-1.31011
10.00	0.02605	0.02048	0.56872	0.01631	-1.28976	-1.29762
8.00	0.09152	0.14168	0.89914	0.04761	-1.27767	-1.23098
7.00	0.18861	0.30443	0.95672	0.07894	-1.26770	-1.19024
6.00	0.41543	0.62092	0.81671	0.11663	-1.25536	-1.18926
5.00	0.90382	1.20144	0.45889	0.09916	-1.23487	-1.44020
4.50	1.24437	0.96841	1.19373	-0.13653	-1.20897	-2.06755
4.00	1.64453	-1.27575	5.47300	-0.84619	-0.86801	- .30554
3.75	1.88349	-1.13125	6.45764	-0.90367	-0.78769	.40946

Table VI. Quantities for spin-orbit matrices

$\Omega = 1/2$	$^2\Sigma^+$	$^2\Pi$
$^2\Sigma^+$	0	$\sqrt{2}\,\lambda$
$^2\Pi$	$\sqrt{2}\,\lambda$	$-\lambda$

$\Omega = 3/2$	$^2\Pi$
$^2\Pi$	$+\lambda$

Ga λ = .001255 au

In λ = .00336

Tl λ = .011835

Table VII.   Spin-orbit coefficients for the $\Omega = 1/2$ states

	$R(a_0)$	C_Σ	C_Π
GaKr	3.75000	.99955	.02998
	4.00000	.99960	.02813
	4.50000	.99961	.02787
	5.00000	.99927	.03811
	6.00000	.99641	.08468
	7.00000	.98199	.18892
	8.00000	.93379	.35782
	10.00000	.82915	.55902
	15.00000	.81649	.57736
InKr	3.75000	.99704	.07690
	4.00000	.99738	.07238
	4.50000	.99742	.07175
	5.00000	.99534	.09644
	6.00000	.98063	.19588
	7.00000	.93712	.34900
	8.00000	.87677	.48091
	10.00000	.82132	.57047
	15.00000	.81649	.57736
TlKr	3.75000	.97505	.22197
	4.00000	.97731	.21180
	4.50000	.97763	.21034
	5.00000	.96502	.26219
	6.00000	.91737	.39803
	7.00000	.86679	.49867
	8.00000	.83612	.54854
	10.00000	.81788	.57540
	15.00000	.81649	.57736

Table VIII.   Rydberg-valence transition moments in GaKr
(with spin-orbit corrections)

| R | III 1/2 - I 1/2 | | III 1/2 - II 1/2 | | III 1/2 - I 3/2 |
	Z	(X,Y)	Z	(X,Y)	(X,Y)
15.00	-0.75641	0.74574	-1.06969	-0.52733	-0.91335
10.00	-0.72540	0.75618	-1.07592	-0.50983	-0.91200
8.00	-0.44047	0.84363	-1.14948	-0.32327	-0.90345
7.00	-0.22486	0.88026	-1.16880	-0.16935	-0.89640
6.00	-0.10071	0.88449	-1.18499	-0.07517	-0.88767
5.00	-0.05489	0.87255	-1.43915	-0.03328	-0.87318
4.50	-0.05762	0.85454	-2.06674	-0.02383	-0.85487
4.00	-0.00859	0.61353	-0.30542	-0.01727	-0.61378

Table IX. Atomic states of Ga , In , and Tl

State	Excitation Energy					
	Ga		In		Tl	
	cm^{-1}	eV	cm^{-1}	eV	cm^{-1}	eV
$^2P_{1/2}$	0.0	0.0	0.0	0.0	0.0	0.0
$^2P_{3/2}$	826.24	.10241	2212.56	.274228	7792.7	.965840
$^1S_{1/2}$	24788.58	3.07234	24372.87	3.020814	26477.5	3.281665
I.P.	48380.	5.9963	46669.93	5.784348	49264.2	6.105886

Table X. Rydberg-to-valence transition moments in model TlKr
(with spin-orbit corrections)

| R | III 1/2 - I 1/2 | | III 1/2 - II 1/2 | | III 1/2 - I 3/2 |
	Z	(X,Y)	Z	(X,Y)	(X,Y)
15.00	-0.75641	0.74574	-1.06969	-0.52733	-0.91335
10.00	-0.74665	0.74590	-1.06130	-0.52476	-0.91200
8.00	-0.67524	0.75539	-1.02925	-0.49558	-0.90345
7.00	-0.59354	0.77699	-1.03169	-0.44701	-0.89640
6.00	-0.47336	0.81433	-1.09099	-0.35332	-0.88767
5.00	-0.37761	0.84264	-1.38982	-0.22894	-0.87318
4.50	-0.43489	0.83575	-2.02130	-0.17981	-0.85487
4.00	-0.06471	0.59985	-0.29861	-0.13000	-0.61378

Table XI. Morse fitting parameters:

$$V(R) - V(\infty) = D_e[u^2 - 2u] \quad \text{where} \quad u = \exp[B(R_e - R)]$$

Molecule	State	D_e	$R_e(a_0)$	$B(a_0^{-1})$
GaKr	$I_{1/2}$	.000772	7.56	.724
	$I_{3/2}$	.00147	7.19	.722
	$II_{1/2}$	.000625	10.14	.471
	$III_{1/2}$	.00295	6.26	.853
InKr	$I_{1/2}$	.000286	7.86	.817
	$I_{3/2}{}^a$			
	$II_{1/2}$	.000474	10.24	.483
	$III_{1/2}{}^a$			
TlKr	$I_{1/2}$	.00439	8.52	.633
	$I_{3/2}{}^a$			
	$II_{1/2}$	.000408	10.12	.502
	$III_{1/2}{}^a$			

[a]Same as for GaKr

Fig. 1. Orbital diagrams for the electronic states of Ga + Kr and Ga[+] + Kr.
The lobes and circles represent the in-plane and out-of-plane p orbitals;
the dashed circle denotes the Rydberg orbital.

THE LOW-LYING ELECTRONIC STATES
OF GaKr AND GaKr[+]
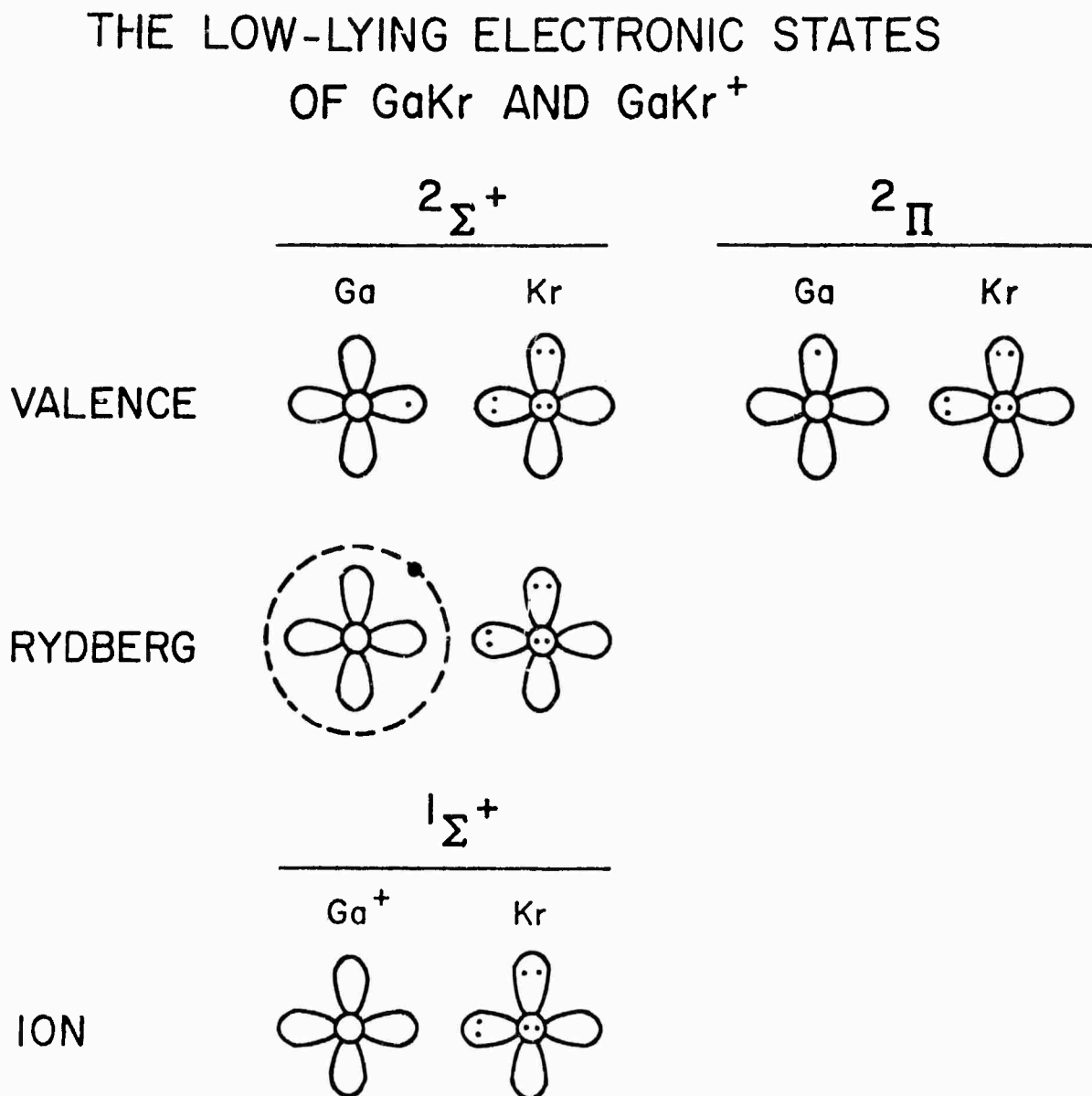
Figure 2.

THE LOW-LYING STATES OF GaKr AND GaKr⁺

Figure 3.

DIPOLE MOMENTS OF THE LOW-LYING STATES OF GaKr
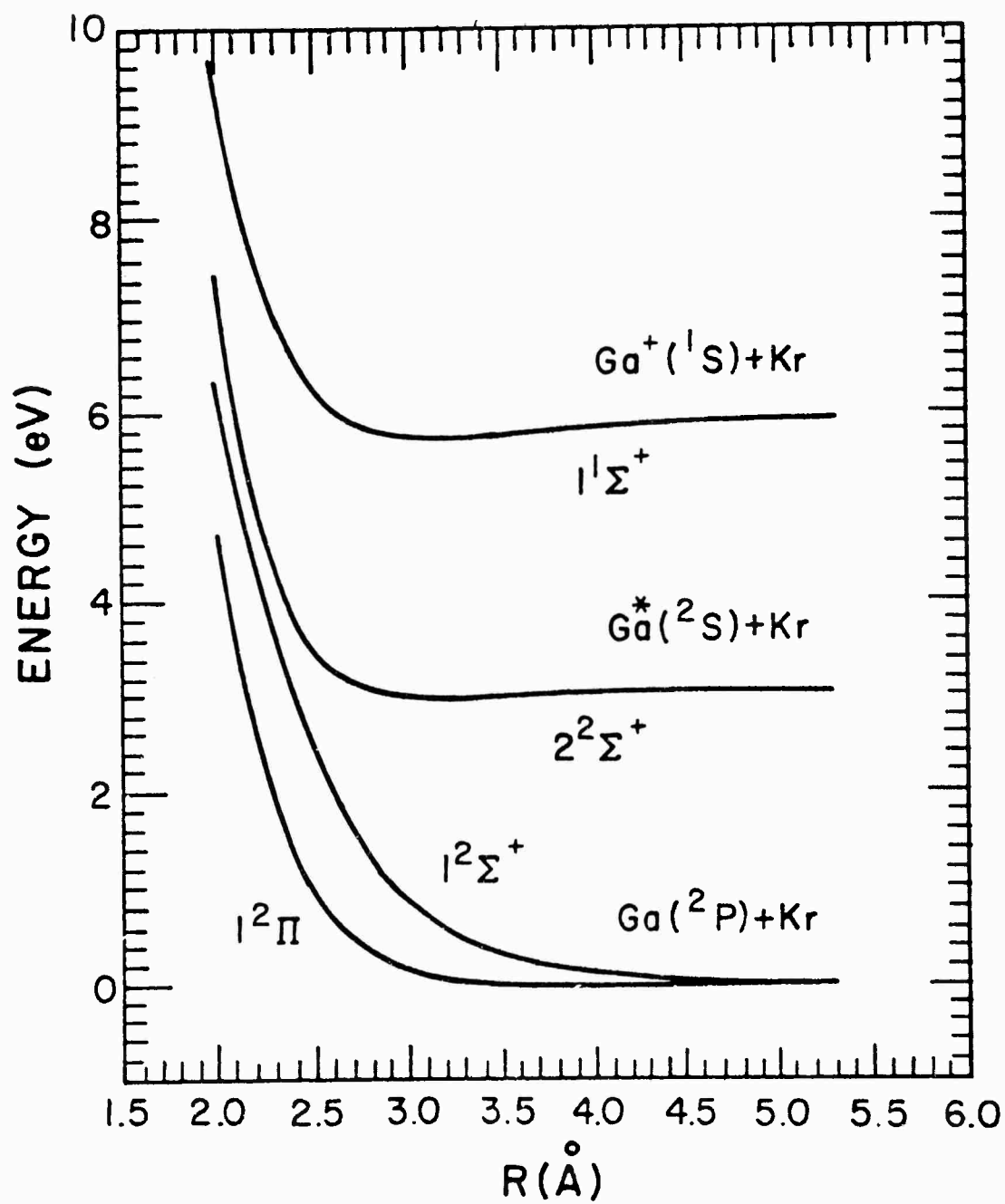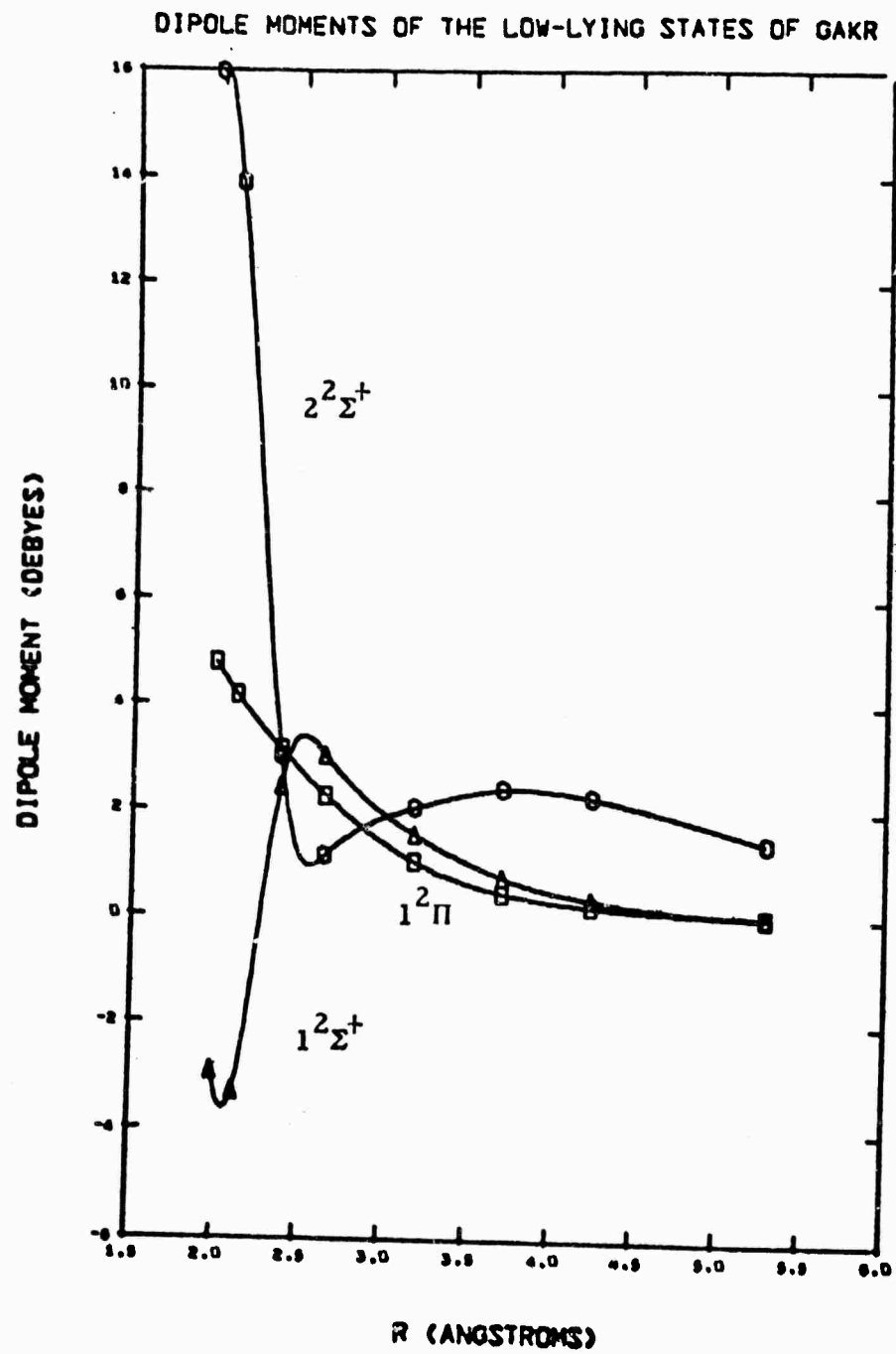
Figure 4.

DIPOLE TRANSITION MOMENTS AMONG
THE LOW-LYING STATES OF GaKr
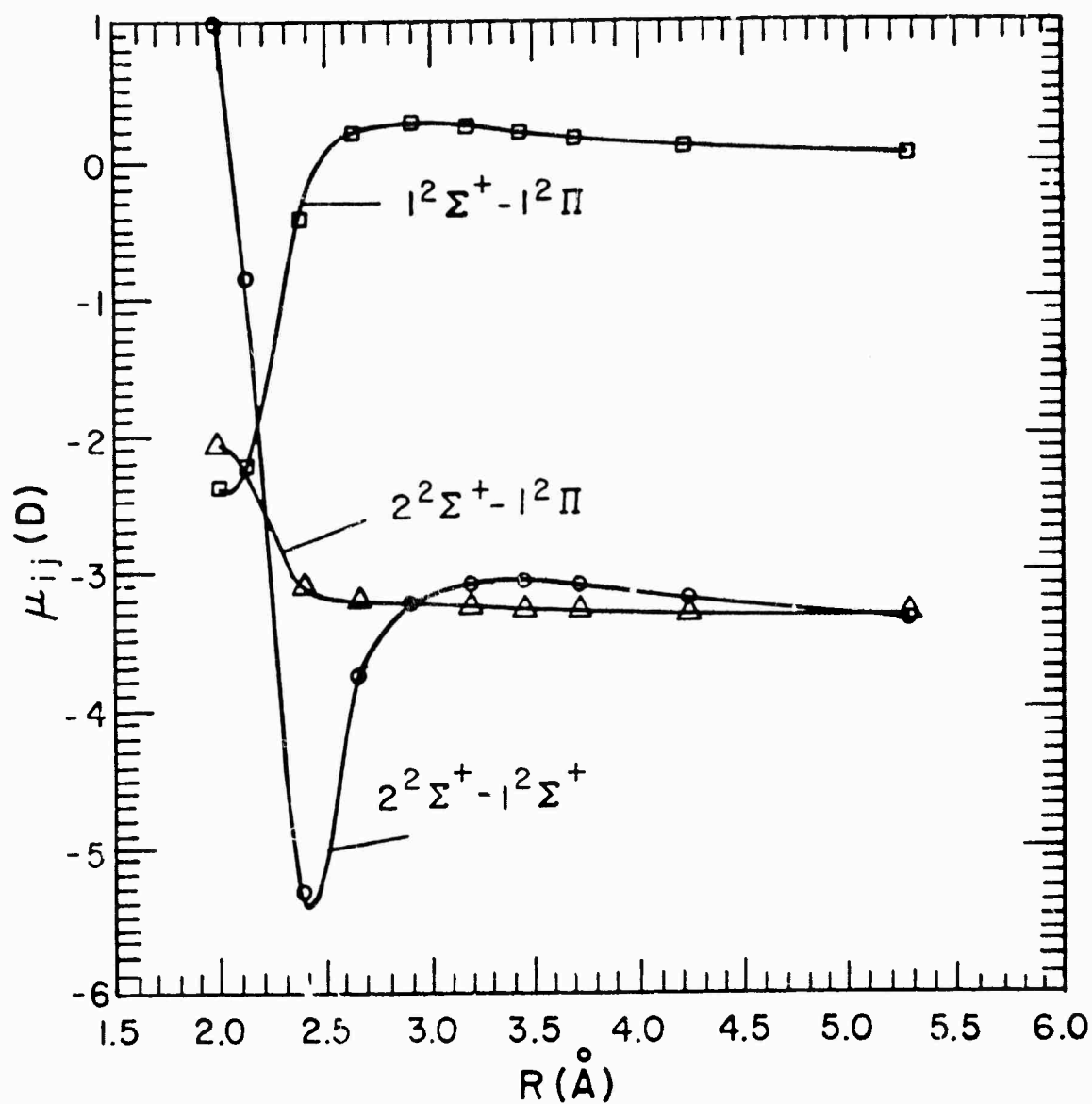
Figure 5.

THE LOW-LYING STATES OF GaKr AND GaKr$^+$ WITH SPIN-ORBIT CORRECTIONS
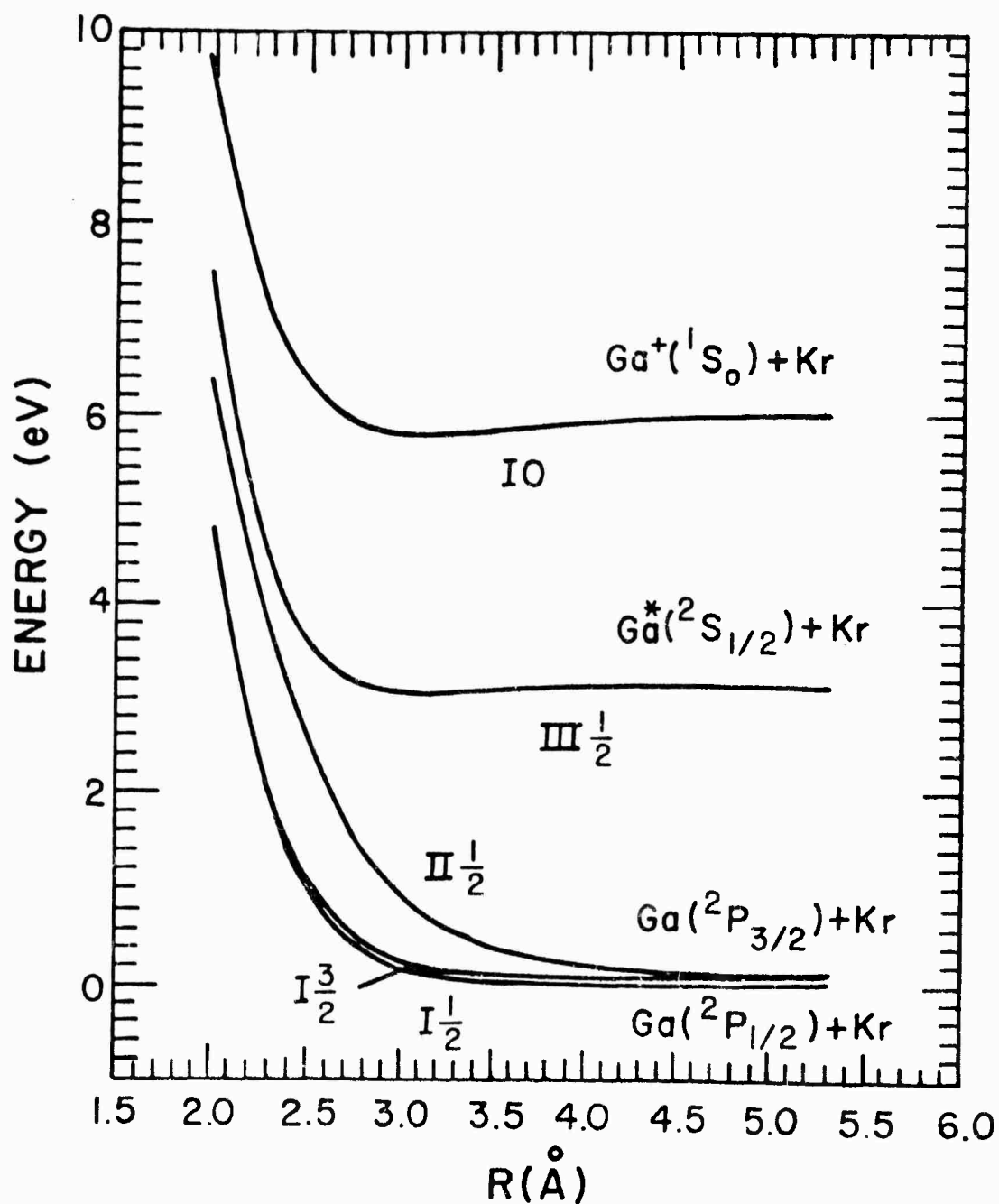
Figure 6.

DIPOLE TRANSITION MOMENTS AMONG THE LOW-LYING STATES OF GaKr WITH SPIN-ORBIT CORRECTIONS
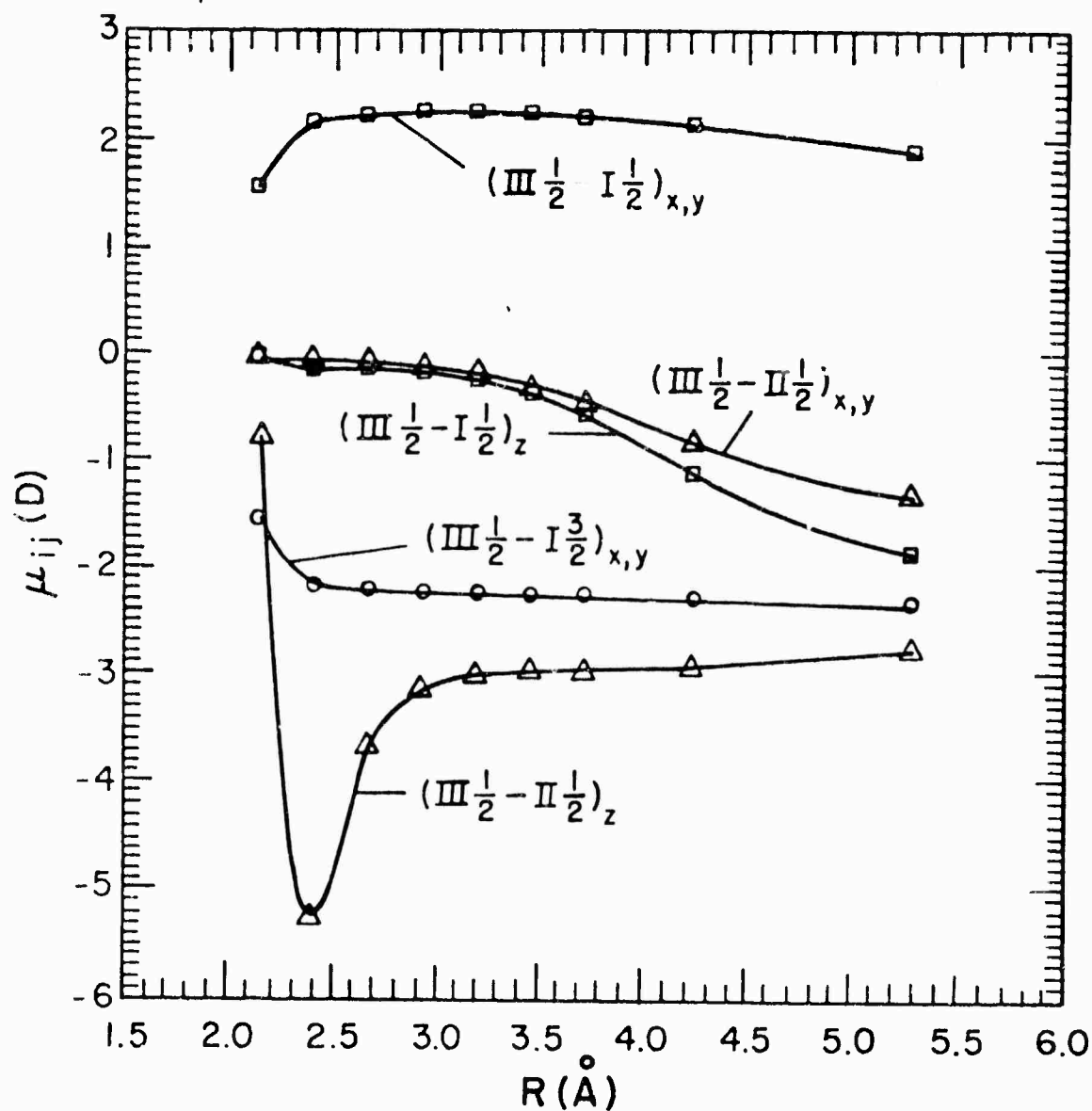
Figure 7.

THE LOW-LYING STATES OF InKr AND InKr$^+$ WITH SPIN-ORBIT CORRECTIONS
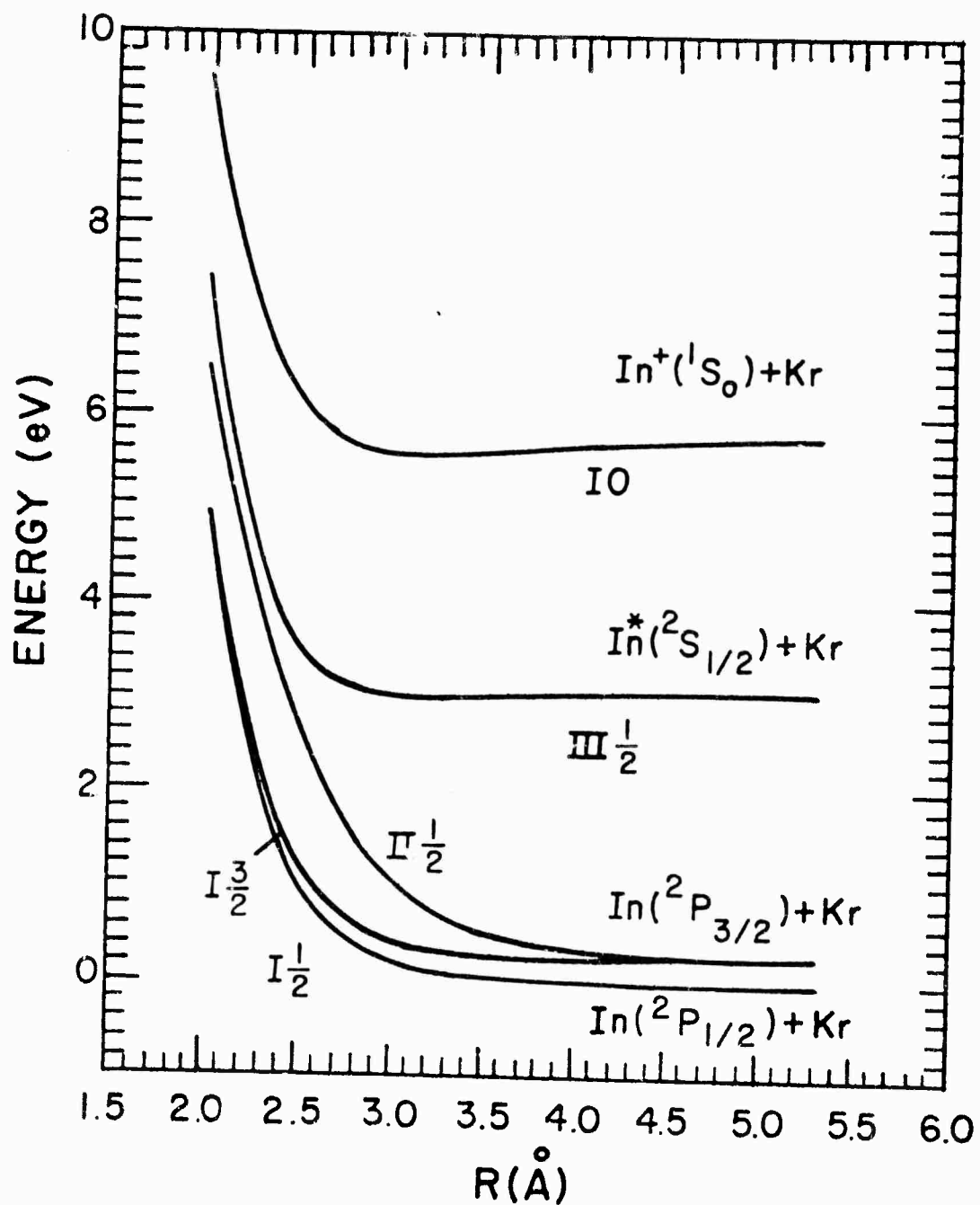
Figure 8.

THE LOW-LYING STATES OF TlKr AND TlKr$^+$ WITH SPIN-ORBIT CORRECTIONS
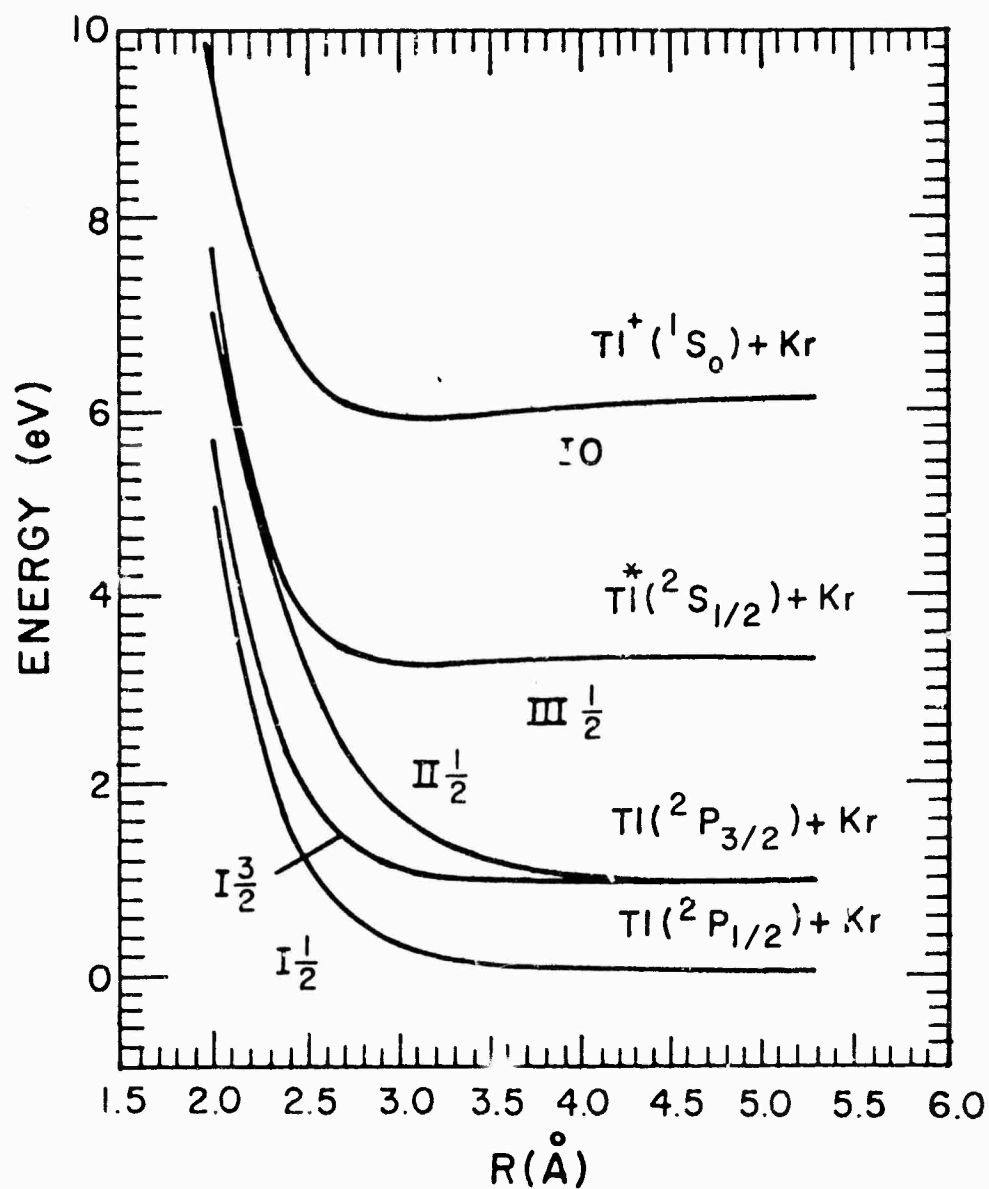
Figure 9.

DIPOLE TRANSITION MOMENTS CONNECTING THE LOW-LYING STATES OF TlKr WITH SPIN-ORBIT CORRECTIONS

$(III\frac{1}{2}-I\frac{1}{2})_{x,y}$

$(III\frac{1}{2}-I\frac{1}{2})_z$ $(III\frac{1}{2}-II\frac{1}{2})_{x,y}$

$(III\frac{1}{2}-I\frac{3}{2})_{x,y}$

$(III\frac{1}{2}-II\frac{1}{2})_z$

$\mu_{ij}(D)$

$R(\overset{\circ}{A})$
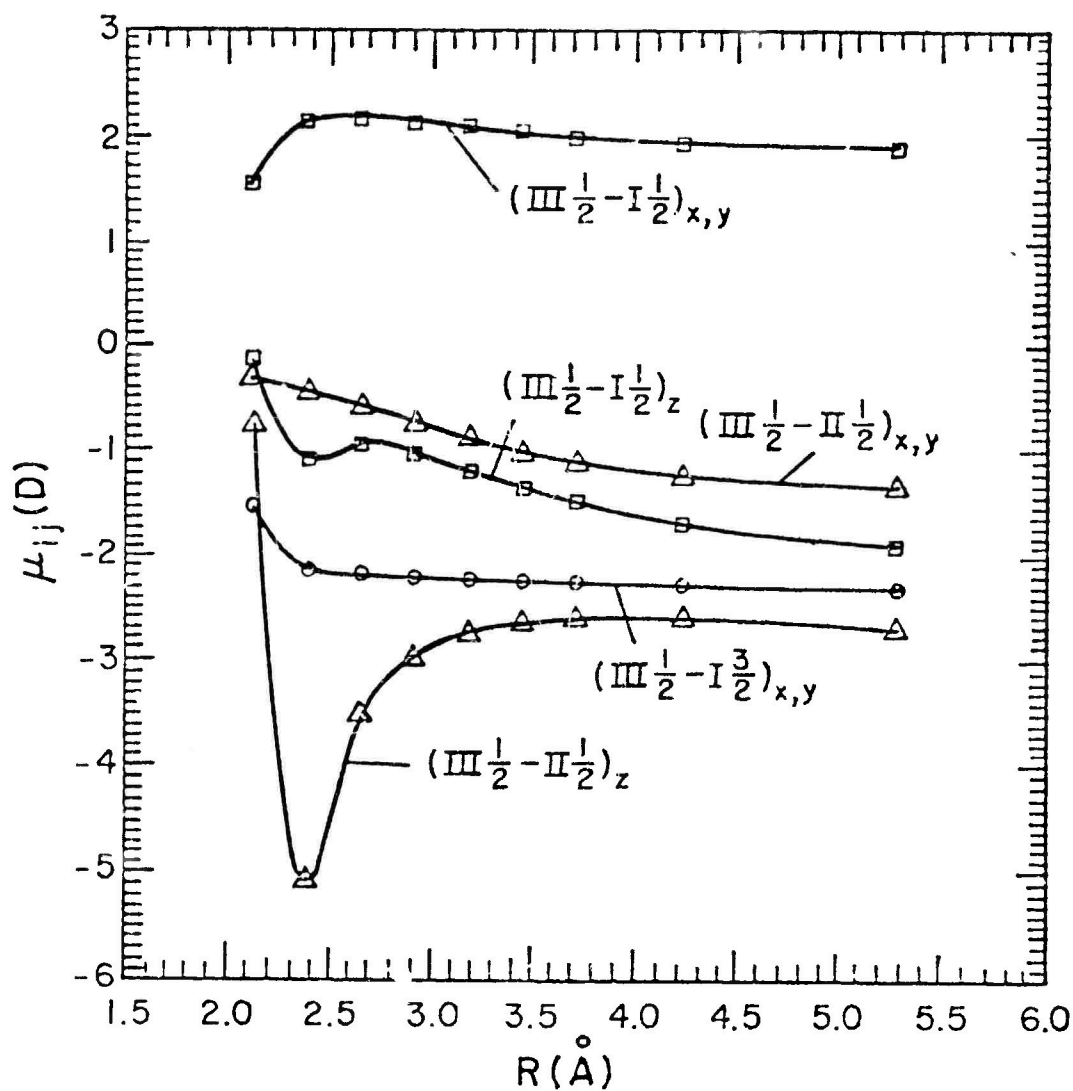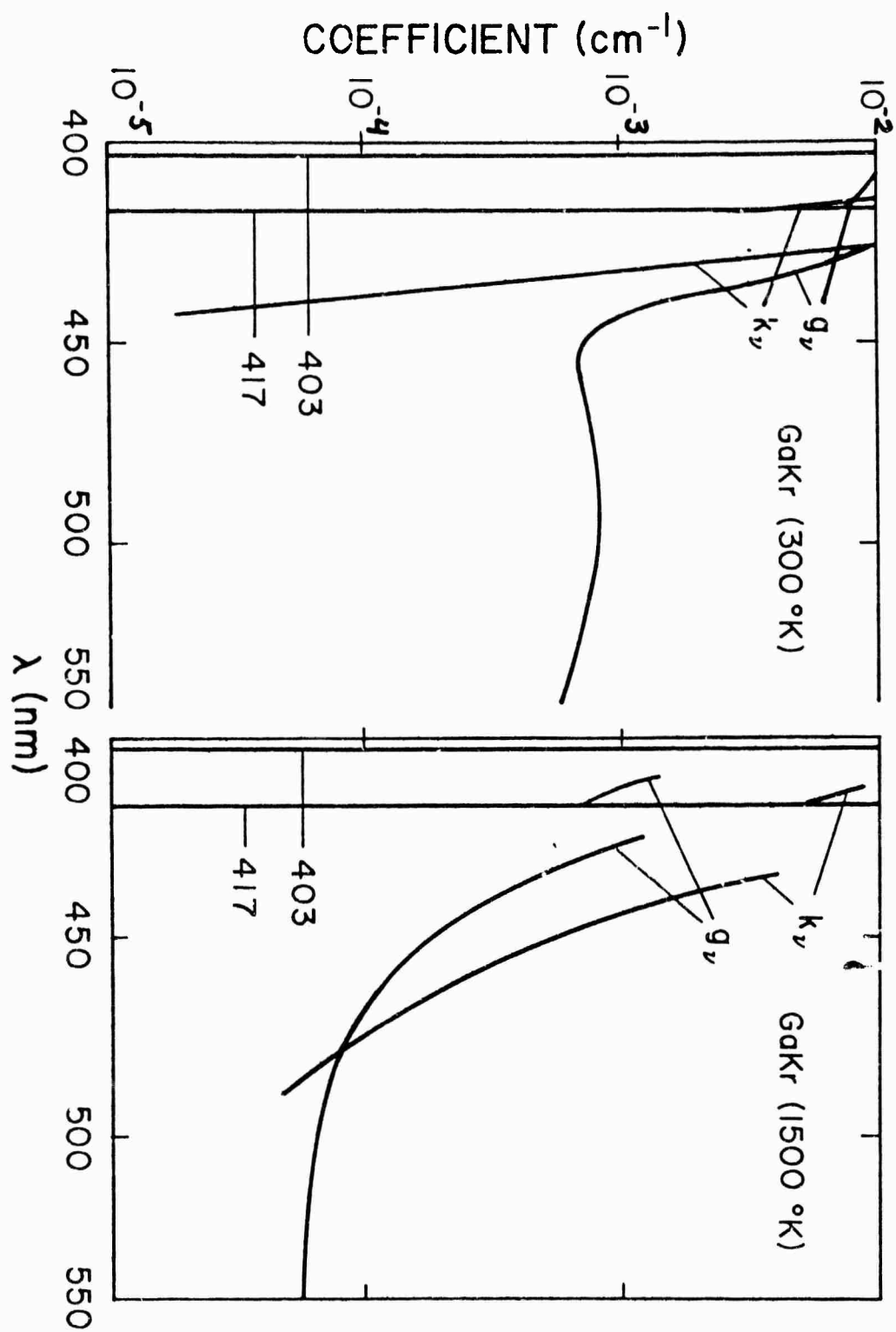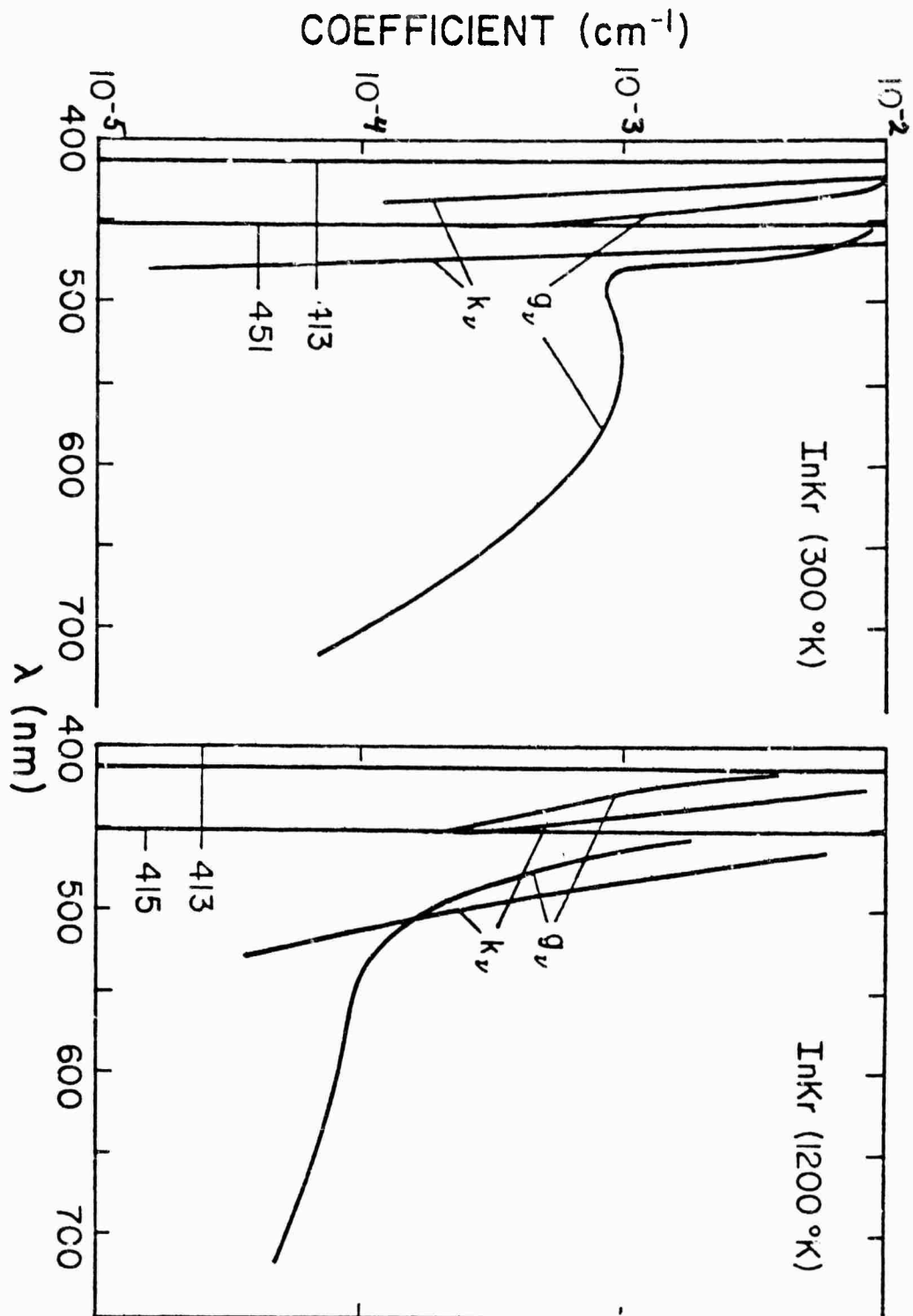
Figure 10.

Figure 11.

Figure 12.
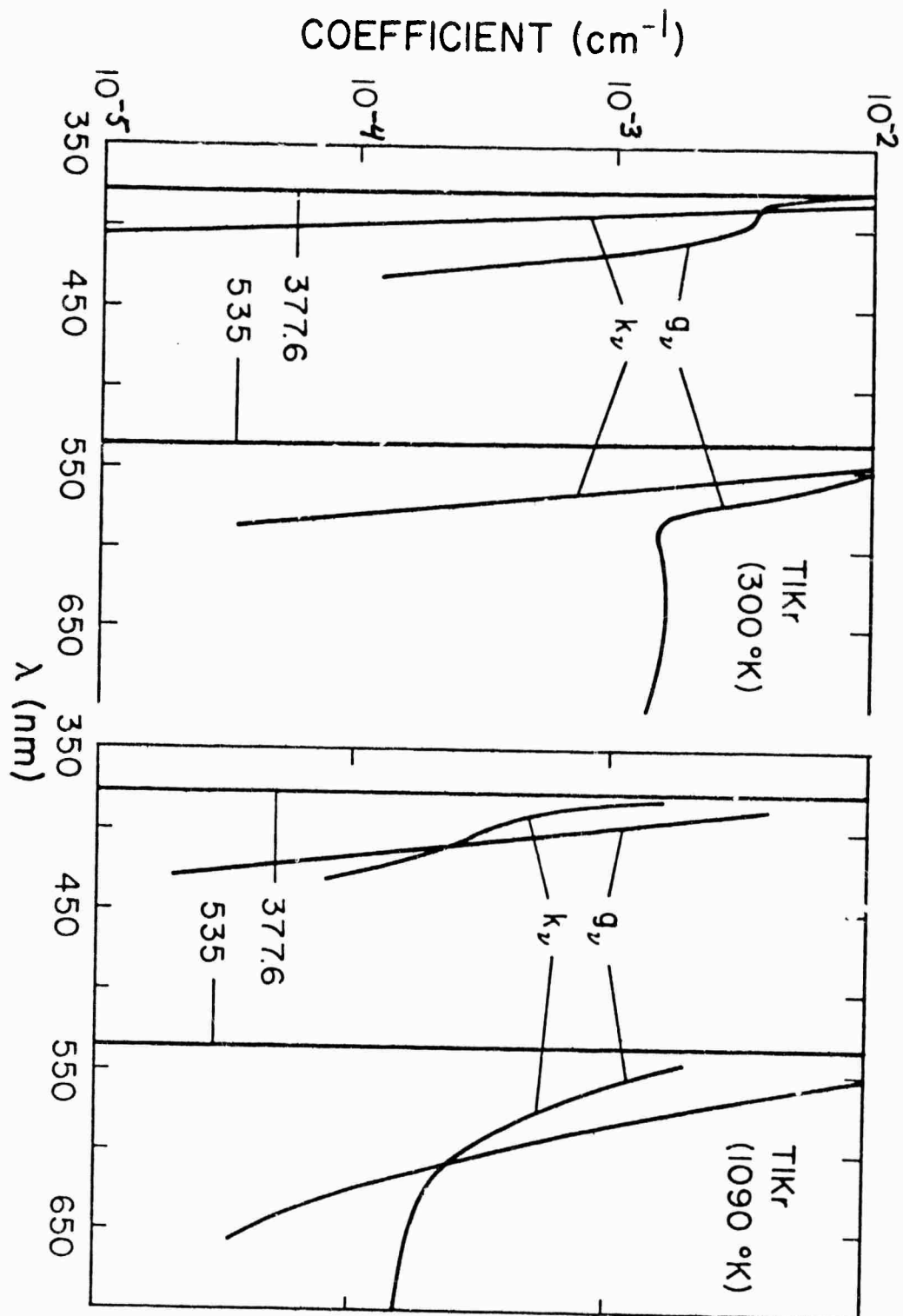
III. Application of the Gordon-Kim theory to the group IIIB-rare gas systems

In recent years, the electron gas methods developed by Gaydaenko and Nikulin [1], and Gordon and Kim [2] and modified by Rae [3] and Cohen and Pack [4] have proved successful in calculating the interaction energies of pairs of closed shell atoms or ions [1-5], of atom-molecule systems[6-7], of molecule-molecule systems [8], and, recently, of systems with one open shell atom [9]. These interaction energies are much more accurate than the simplicity of the Gordon-Kim (GK) method would lead one to expect.

The recent success of the GK method in calculating closed shell - open shell interaction energies has prompted us to use this method to calculate the interaction of group IIIB-noble gas pairs. The GK theory has been most successful in cases where the interaction is non-covalent and where the atoms are relatively undistorted. For these reasons, systems such as GaKr would seem to be ideal candidates for a GK calculation.

The electron-gas theory is briefly reviewed in part A, and our preliminary results on GaKr are given in part B.

A. The electron gas method

The method we have used is that of Gordon and Kim [2] as modified by Cohen and Pack [4]. A more detailed description of the theory is available in these two papers. Briefly the GK theory approximates the intermolecular

potential V(R) at the distance R by

$$V(R) \simeq V^{GK}(R) = V_{HF}^{GK}(R) + V_{corr}^{GK}(R)$$

where

$$V_{HF}^{GK} = V_k + V_c + V_e$$

and these three terms represent the kinetic, Coulomb and exchange inter-
action energies, respectively. To calculate these interaction energies,
the electronic charge density ρ is approximated by the sum of the atomic
charge densities,

$$\rho \simeq \rho_a + \rho_b .$$

With this approximation, the Coulomb interaction can be calculated directly,
but the other terms are all estimated by the formulas for the energy density
of a uniform electron gas [4]. An additional modification [3,4] is made
to the exchange energy to avoid self-exchange contributions.

B. Calculations

We have modified the molecule-molecule GK interaction program of
Parker, Snow and Pack [8], which allows for non-spherical potentials, to
calculate interaction energies for closed shell - open shell atomic pairs.
The density of the open shell atom, in this case Ga , is divided into

the spherically symmetric core density plus the valence density. For Ga in the ground state $(4s^2 4p^1)$, the valence density is constrained to be in a p orbital directed along the internuclear axis, to form a Σ molecular state, or perpendicular to it to form a Π state.

In order to expedite the evaluation of integrals, the atomic density is expanded in a set of Slater basis functions with the coefficients determined by a least-squares fit [4]. The basis set expansions for the density are then read into the GK program which calculates the interaction energy by three-dimensional numerical quadriture.

We have obtained numerically tabulated, relativistic Hartree-Fock densities for the group IIIB and rare gas atoms from Joseph Mann [10]. The densities of the $4s^2 4p^1$ and $4s^2 5s^1$ states of Ga and the ground state of Kr were fit with small sets of Slater functions. At this time the fit of the basis set expansion is not very good ($\sim 10\%$).

The basis set expansions obtained from this fitting procedure were then used to calculate the GK interaction energies. Because the fitting procedure does not normalize the density, the inaccuracy of the present expansions results in a spurious Coulomb repulsion between the two atoms. We hope that improving the basis set fit will correct this error.

The GK potential curves are compared with the CI results (see Section II) in Figures 1-3. The energies are plotted with respect to the asymptotic energy of each state. The curve labeled GKR includes Rae's correction while the GK curve is the unmodified GK theory. The GKR curve for the $1^2\Sigma^+$ state agrees remarkably well with the CI result. Unfortunately, the agreement for both the $1^2\Pi$ and $2^2\Sigma^+$ states are not as good. Specifically the depths and positions of the potential wells are not predicted accurately. We are currently working on improving the basis set fit and thereby the interaction energies.

GaKr 1²Π
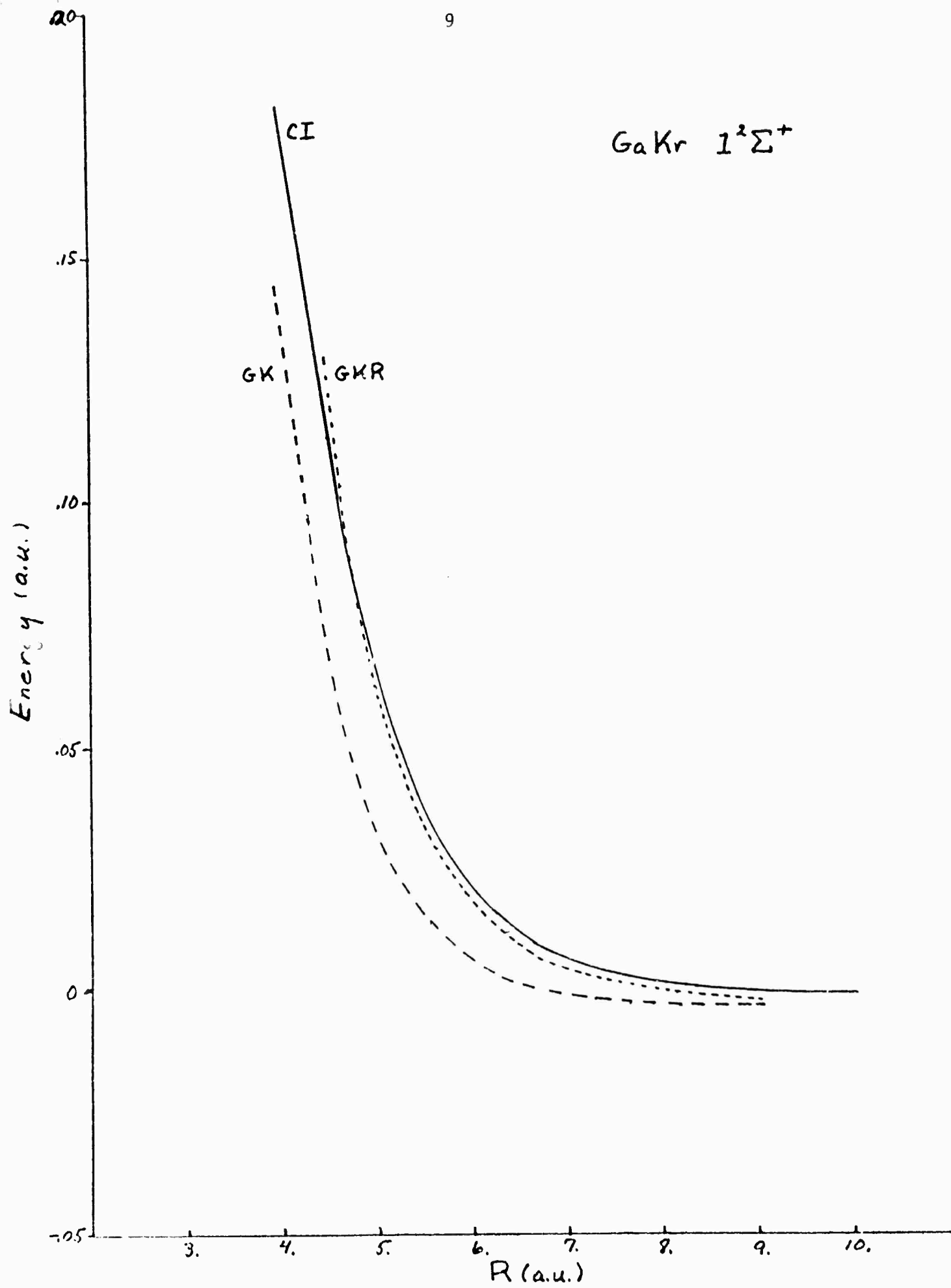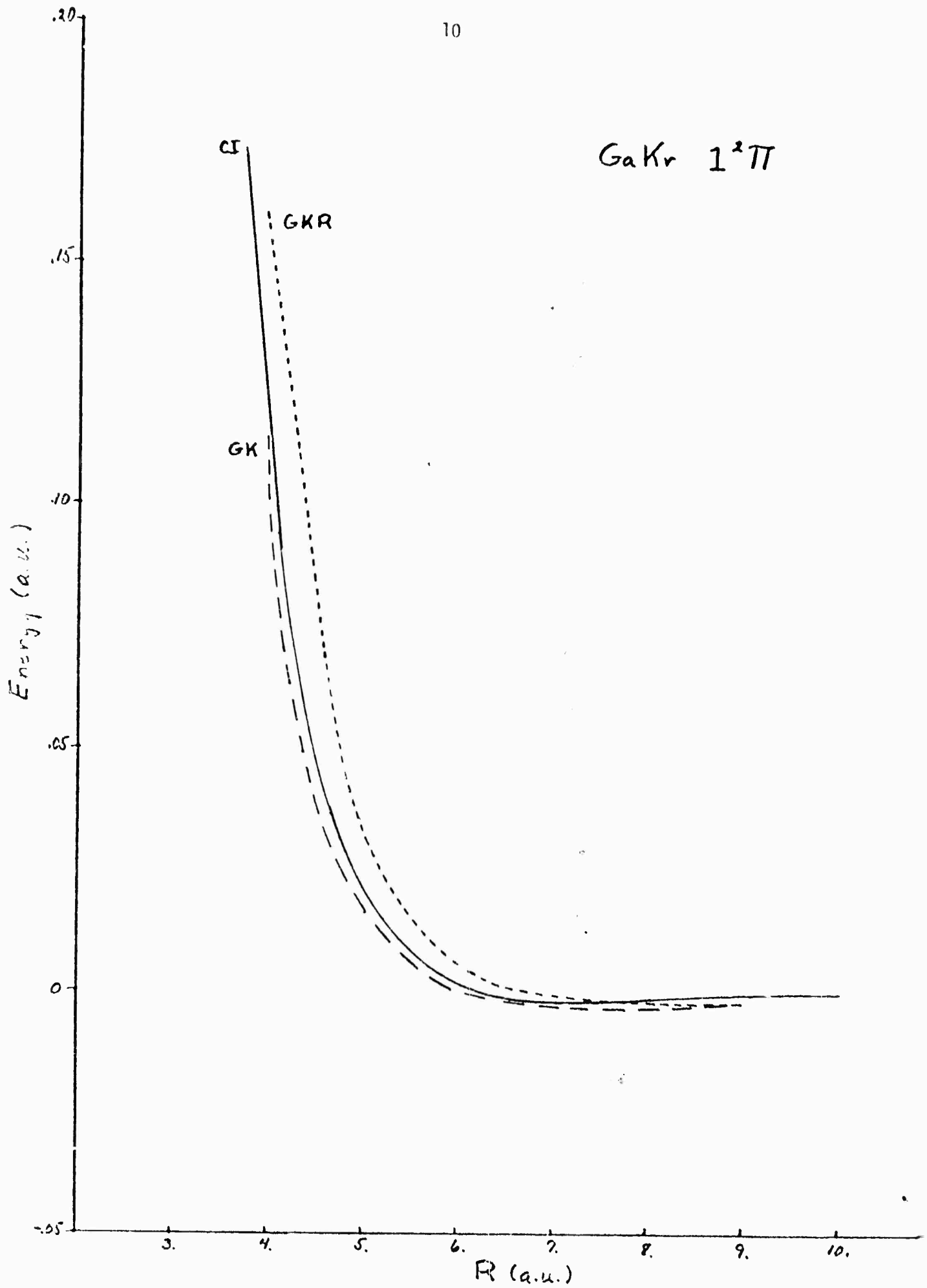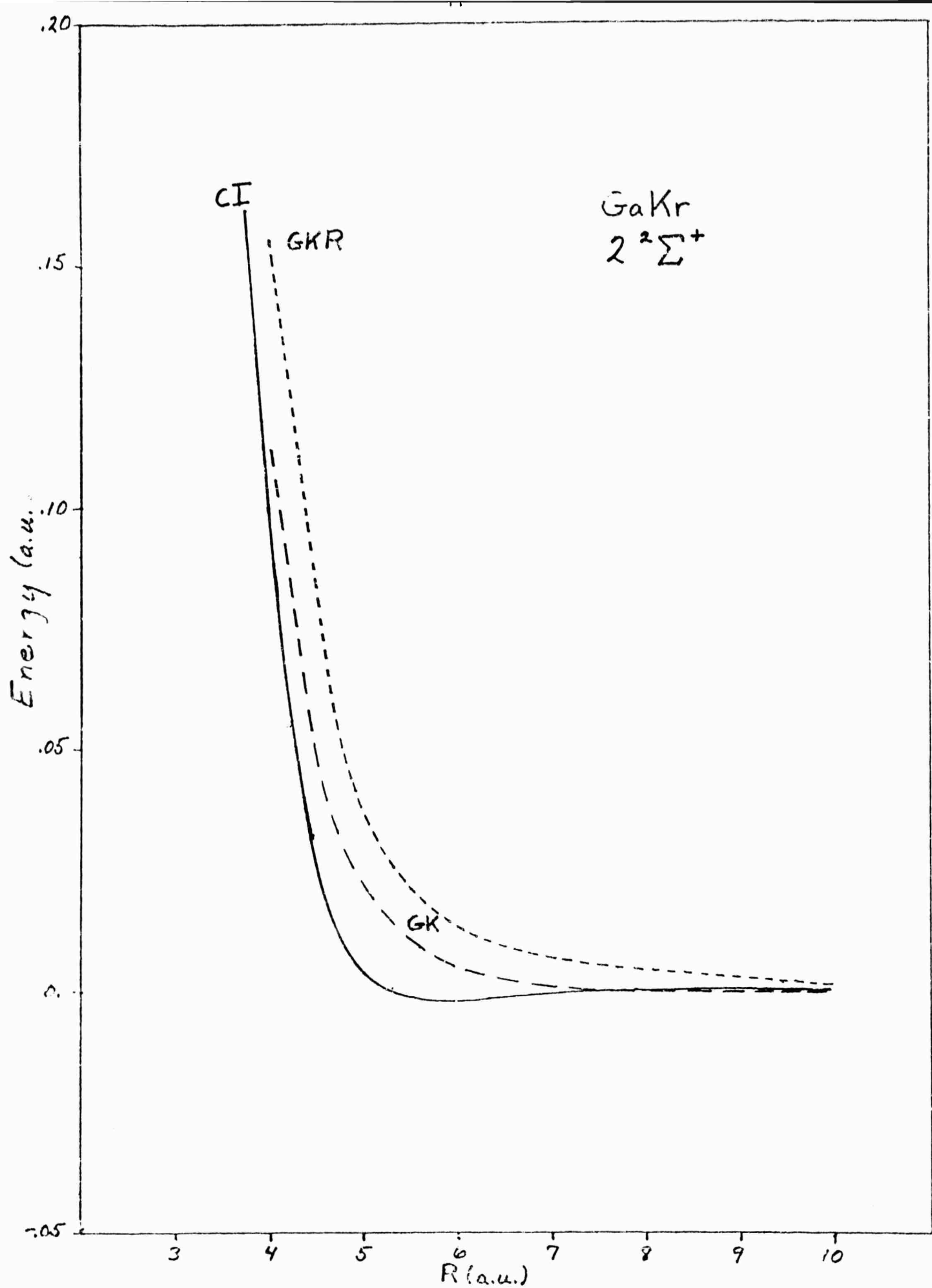
1. V. I. Gaydaenko and V. K. Nikulin, Chem. Phys. Letters $\underline{7}$, 360 (1970); V. K. Nikulin, Zh. Tekh, Fiz. 41, 41 (1970) [English transl. Soviet Phys. Tech. Phys. $\underline{16}$, 28 (1971)].

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10. Joseph Mann, private communication.

IV. The Electron Scattering Model

A. Introduction

This section describes the theoretical basis of our calculations
using the electron scattering model. For an excimer system AB , where
A is a closed-shell system, most of the states of interest correspond
to the asymptotic situation where B is excited but A is in its ground
state. Fundamentally, what the electron scattering theory says is that any
charged particle in B sees a potential (Σ_A) , due to the closed-shell
system A , which is the same as if the charged particle were scattered
off of A . This scattering potential is corrected for the fact that A
is "de-polarised" relative to the scattering problem, due to the presence
of the nucleus and other electrons of B . This theory is based on the
model interaction potentials and response functions that arise out of the
many body theory (using Schwinger Functional Derivatives) and that have
been applied to scattering problems [1].

In part B the basic equations are presented and possible methods
for calculating the interaction energy are discussed in part C. The use
of semiempirical forms for the effective potentials are discussed in
part D.

B.   The Basic Equations

Using many-body field theoretic methods it has been shown that the change in energy, ε , resulting from the addition of an electron to a closed-shell reference system (referred to here as A) is given by the one-particle Dyson equation

$$T(r)\phi(r) + \int dr' \; \Sigma^A(r;r':\varepsilon)\phi(r) \;\; = \;\; \varepsilon\phi(r) \tag{1}$$

where T is the kinetic energy operator and ϕ is the Dyson amplitude with r and r' being space-spin coordinates. Thus, the problem reduces to an effective one-particle problem in which this particle experiences an effective potential, Σ^A , which represents all the other particles collectively, taking into account all effects such as polarization, correlation and exchange, etc. As might be expected, the cost of this simple formulation is that Σ^A is an extremely complicated entity which is both nonlocal and energy dependent and which cannot rigorously be brought into closed form. However, it has been possible to develop

excellent closed form approximations to this potential which are based on well founded physical concepts. Most notable among these is the Random Phase Approximation (RPA) potential, Σ_{RPA}, which has been very successfully used : calculating the ionization potentials, excitation energies, oscillator strengths, and elastic-scattering phase shifts for He [2]. Σ_{RPA} has also been used to accurately calculate the ionization and excitation energies of Li [3]. Moreover, it has been shown that this ab initio potential encompasses other phenomenologically derived semiempirical potentials which have be n used by other workers with great success [4].

It has also been recently demonstrated that by applying the same many-body techniques to the problem of two electrons added to a closed-shell reference system (A) one obtains an effective two-particle equation for the resulting change in energy [5]

$$[\sum_{i=1}^{2}\left(T(r_i) + \int dr' \Sigma^A(r_i;r_i':\epsilon)\right) + \frac{1}{|r_1-r_2|} + \int dr_1'dr_2' W^A(r_1,r_2;r_1'r_2')]\Phi(r_1,r_2) =$$

$$\epsilon\Phi(r_1,r_2) , \tag{2}$$

where in addition to the individual one-particle potentials there now appears a two-particle effective potential, W^A, which represents how the presence of one particle affects the potential seen I the other particle and which reflects the fact that system A can act as a dielectric medium to shield the Coulombic interaction between two charged particles. As with Σ^A, this potential cannot be rigorously brought into closed form.

However, an excellent <u>ab initio</u> closed form approximation to this potential can be obtained with the Random Phase Approximation, W_{RPA} , which is completely compatible with the similarly obtained one-particle potential, Σ_{RPA} .

If we now proceed to the case of adding m electrons to our closed-shell reference system it follows by induction and can be proven formally that the change in energy is given by

$$
\begin{aligned}
&\left[\sum_{i=1}^{m} \left(T(r_i) + \int dr_i' \; \Sigma^A(r_i;r_i':\epsilon) \right) + \sum_{i>j}^{m} \left(\frac{1}{|r_i-r_j|} + \int dr_i' \; dr_j' \; W^A(r_i r_j;r_i',r_j':\epsilon) \right) \right. \\
&\left. + \sum_{i>j>k}^{m} \int dr_i' \; dr_j' \; dr_k' \; U^A(r_i,r_j,r_k;r_i',r_j',r_k':\epsilon) + \ldots + \int dr_1' \; \ldots \; dr_m' V^A(r_1 \ldots r_m;r_1' \ldots r_m':\epsilon) \right] \Psi(r_1 \ldots r_m) \\
&= \epsilon \Psi(r_1 \ldots r_m) \; , \qquad\qquad\qquad\qquad (3)
\end{aligned}
$$

where our notation for three-particle and higher potentials is obvious.

In the above we only considered the addition of electrons to our closed-shell reference system A. However, we can also add nuclei as well; the only difference being that when acting on a nuclear coordinate all potential terms involving electron exchange must of course vanish. Since this can be trivially accomplished by choosing an appropriate (artificial) nuclear spin coordinate, we can immediately generalize (3) to include both nuclei and electrons by allowing the particles to carry different charges, z , (where $z = -1$ for an electron) to give

$$[\sum_{i=1}^{m}(T(r_i) - z_i \int dr_i' \Sigma^A(r_i;r_i':\epsilon)) + \sum_{i>j}^{m} z_i z_j (\frac{1}{|r_i-r_j|} + \int dr_i' dr_j' W^A(r_i,r_j;r_i',r_j':\epsilon))$$

$$+ \ldots] \psi(r_1 \ldots r_m) = \epsilon \psi(r_1 \ldots r_m) . \tag{4}$$

We of course cannot solve (4) since the potentials involved cannot be written in closed form. However, we can replace these potentials by their RPA approximates which are in closed form. Furthermore, realizing that we are deriving a theory for intermolecular forces which is essentially perturbative in nature, we will now assume that all three-particle and higher potentials can be neglected so that our equation becomes simply

$$[\sum_{i=1}^{m}(T(r_i) - z_i \int dr_i' \Sigma^A(r_i;r_i':\epsilon)) + \sum_{i>j}^{m} z_i z_j (\frac{1}{|r_i-r_j|} + \int dr_i' dr_j' W^A(r_i,r_j;r_i',r_j':\epsilon))] \psi(r_1 \ldots r_m)$$

$$= \epsilon \psi(r_1 \ldots r_m) . \tag{5}$$

Since our interest lies in the calculation of potential energy surfaces, what we really want is an equation for the change in energy when m_e electrons and m_n nuclei are added to A with these nuclei held fixed at specific points in space (which we will refer to collectively as R with the actual spatial coordinate of nuclei i being R_i). That is, we want to be able to separate electronic motion from nuclear motion so that this quantity, $\mathcal{E}(R)$, will be the total potential experienced by these nuclei and will satisfy the equation

$$[\sum_{i=1}^{m_n} T(R_i) + \mathcal{E}(R)] X(R) = \epsilon X(R) \tag{6}$$

where $X(R)$ is a function of the nuclear coordinates only. As it stands, (5) precludes such a separation because of the energy dependence of the potentials involved. To overcome this problem we will now assume that for those solutions to (5) we seek this energy dependence is not strong Furthermore, we will also assume that the response of A to the added particles is instantaneous. In this way we can replace the non-adiabatic energy dependent potentials in (5) with their hermitian energy independent adiabatic approximates such as those given in ref. 5. With these substitutions (5) does become separable, and by taking

$$\Psi(r_1 \ldots r_m) = \sum_j X_j(R) \psi_j(r_1 \ldots r_{m_e}) \; ; \; \langle \psi_i | \psi_j \rangle = \delta_{ij} \tag{7}$$

where $\psi(r_1 \ldots r_{m_e})$ is a function of only the electronic coordinates we find that $\mathcal{E}(R)$ is given by

$$\mathcal{E}(R) = E^A(R) - \sum_{i=1}^{m_n} z_i \, \Sigma^A(R_i) + \sum_{i>j}^{m_n} z_i z_j \left(\frac{1}{|R_i - R_j|} + W^A(R_i, R_j) \right), \tag{8}$$

where E^A is given by the equation

$$[H(r_1 \ldots r_{m_e}; R) + \sum_{i=1}^{m_e} (\int dr_i' \Sigma^A(r; r') - \sum_{j=1}^{m_n} z_j \int dr_i' W^A(r_i, R_j; r_i'))$$

$$+ \sum_{i>j}^{m_e} \int dr_i' dr_j' W^A(r_i, r_j; r_i' r_j')] \, \psi(r_1 \ldots r_{m_e}) = E^A(R) \, \psi(r_1 \ldots r_{m_e}) \tag{9a}$$

where H is the usual hamiltonian for m_e electrons in the field of m_n fixed nuclei

$$H(r_1 \ldots r_{m_e} ; R) = \sum_{i=1}^{m_e} (T(r_i) - \sum_{j=1}^{m_n} \frac{z_j}{|r_i - R_j|}) + \sum_{i>j}^{m_e} \frac{1}{|r_i - r_j|}$$

$$= \sum_{i=1}^{m_e} h(r_i) + \sum_{i>j}^{m_e} \frac{1}{r_{ij}} \qquad (9b)$$

and where all one- and two-particle effective potentials are taken to be hermitian adiabatic approximates to the true potentials. Note also that all potential terms involving the m_n nuclei are now written as local quantities thereby taking into account the previously mentioned fact that there are no exchange (i.e. nonlocal) terms in the potentials when nuclei are being considered.

If we now collectively refer to these m_e electrons and m_n nuclei which have a fixed internuclear geometry as being system B, then $\mathcal{E}(R)$ is the change in energy resulting from the creation of system B in the vicinity (as measured by R) of A. If $R \to \infty$ then $\mathcal{E} \to \mathcal{E}_B^o$ which is just the energy B itself. Therefore, the intermolecular potential of the system A-B as a function of the separation between A and B is

$$V_B^A(R) = E_B^A(R) - E_B^0 + V_{B,nuc}^A(R) \qquad (10a)$$

where

$$V_{B,nuc}^A(R) = - \sum_{i=1}^{m_n} z_i^B \sum_{}^{A}(R_i) + \sum_{i>j}^{m_n} z_i^B z_j^B W^A(R_i, R_j) \qquad (10b)$$

and where

$$E_B^0 = \mathcal{E}_B^0 + \sum_{i>j}^{m_n} z_i^B z_j^B \frac{1}{|R_i - R_j|} \tag{10c}$$

is just the electronic energy of isolated system B and where $E_B^A(R)$ is given by

$$[H(r_1 \ldots r_{m_e}; R) + \sum_{i=1}^{m_e} \int dr_i' (\Sigma^A(r_i; r_i') - \sum_{j=1}^{m_n} z_j^B W^A(r_i, R_j; r_i'))$$

$$+ \sum_{i>j}^{m_e} \int dr_i' dr_j' W^A(r_i, r_j; r_i' r_j')] \, \psi_B^A(r_1 \ldots r_{m_e}) = E_B^A(R) \, \psi_B^A(r_1 \ldots r_{m_e}) \tag{10d}$$

Therefore, given that we know E_B^0 and that we have available good closed form adiabatic approximates for Σ^A and W^A our problem reduces to finding the solutions (or rather a particular solution) to (10d). In the following section we will look at some ways of doing this.

C.   Determination of E_B^A

Our equation for E_B^A is of the form

$$(H + U^A) \, \psi_B^A \;=\; E_B^A \, \psi_B^A \tag{11a}$$

where

$$U^A(r_1 \ldots r_{m_e}; R) \;=\; \sum_{i=1}^{m_e} \int dr_i' [\Sigma^A(r_i; r_i') - \sum_{j=1}^{m_n} z_j^B W^A(r_i, R_j; r_i')]$$

$$+ \; \sum_{i>j}^{m_e} \int dr_i' dr_j' W^A(r_i, r_j; r_i', r_j')$$

$$=\; \sum_{i=1}^{m_e} p^A(r) + \sum_{i>j}^{m_e} q_{12}^A(r_i, r_j) \tag{11b}$$

where we note that ψ_B^A is an eigenfucntion of the hermitian 'hamiltonian' $(H + U^A)$ ana that H is the electronic hamiltonian for isolated system B. If we now explicitly assume that U^A is small compared to H (this of course was implicit in our derivation of U^A in the first place) then U^A can be regarded as being a small perturbation on H. As a consequence, the solution, ψ_B^A, to (11) which we seek should resemble the electronic wavefunction for isolated system B, ψ_B^O, and this wavefunction should therefore provide us with a proper starting point determining ψ_B^A and E_B^A.

1.   First-Order Perturbation Treatment

Projecting (11a) against ψ_B^A and normalizing ψ_B^A to unity gives

$$E^A_B = \langle \psi^A_B | H + U^A | \psi^A_B \rangle \; ; \; \langle \psi^A_B | \psi^A_B \rangle = 1 \, , \tag{12a}$$

whereas if ψ^O_B is a self-consistent solution for isolated system B its energy is

$$E^O_B = \langle \psi^O_B | H | \psi^O_B \rangle \; ; \; \langle \psi^O_B | \psi^O_B \rangle = 1 \, . \tag{12b}$$

If we assume that U^A is a quite small perturbation to H then we can solve for E^A_B using standard first-order perturbation theory to obtain

$$E^A_B = E^O_B + \langle \psi^O_B | U^A | \psi^O_B \rangle \tag{13}$$

so that our first-order perturbative expression for V^A_B is simply

$$V^A_B = V^A_{B,nuc} + \langle \psi^O_B | U^A | \psi^O_B \rangle \, . \tag{14}$$

This of course is equivalent to assuming that the wavefunction for system B remains virtually unchanged when in the presence of A .

In terms of the one- and two-particle density matrices, ρ^O_1 and ρ^O_2 , associated with ψ^O_B , (14) becomes

$$V^A_B = V^A_{B,nuc} + \int_{r'=r} dr \; p^A(r') \rho^O_1(r;r') + \int_{r'=r} dr_1 dr_2 \; q^A_{12}(r'_1,r'_2) \rho^O_2(r_1,r_2;r'_1 r'_2). \tag{15}$$

If ψ^O_B is a single Slater determinant so that

$$\rho_2^0(r_1,r_2;r_1',r_2') = 1/2[\rho_1^0(r_1;r_1')\rho_1^0(r_2;r_2') - \rho_1^0(r_1;r_2')\rho_1^0(r_2;r_1')] \quad (16a)$$

with

$$\rho_1^0(r;r') = \sum_{i=1}^{n} \phi_i^\star(r)\,\phi_i(r') \quad (16b)$$

where $\{\phi_i\}$ are the n one-electron spin-orbitals comprising ψ_B^0, then V_B^A takes on the form

$$V_B^A = V_{B,nuc}^A + \sum_{i=1}^{n} \langle\phi_i|p^A|\phi_i\rangle + 1/2 \sum_{i\neq j}^{n} [\langle\phi_i\phi_j|q_{12}^A|\phi_i\phi_j\rangle - \langle\phi_i\phi_j|q_{12}^A|\phi_j\phi_i\rangle]$$

$$(17)$$

where the two-electron integrals over q_{12}^A are written in the standard $\langle 12\|12\rangle$ notation.

If ψ_B^0 cannot be written as a single Slater determinant but can be written as a linear combination of determinants involving n one-electron spatial orbitals $\{\phi_i^0\}$ then (12b) can always be written as

$$E_B^0 = \sum_{i,j}^{n} D_i^j \langle\phi_i^0|h|\phi_j^0\rangle + \sum_{i,j,k,l}^{n} D_{ij}^{kl} \langle\phi_i^0\phi_j^0|\frac{1}{r_{12}}|\phi_k^0\phi_l^0\rangle \quad (18)$$

where $\{D_i^j, D_{ij}^{kl}\}$ are fixed coefficients which depend on the precise form of ψ_B^0 and on orbital overlaps. Since U^A is of the same form as H and, like H, is spin independent (recall that isolated system A must be closed-shell) we can immediately write our first-order approximation for V_B^A as

$$V_B^A = V_{B,nuc}^A + \sum_{i,j}^n D_i^j <\phi_i^0|p^A|\phi_j^0> + \sum_{i,j,k,l}^n D_{ij}^{kl} <\phi_i^0\phi_j^0|q_{12}^A|\phi_k^0\phi_l^0> \qquad (19)$$

where all operators and integrals are now explicitly takent to involve only spatial coordinates. Therefore, we can determine $<\psi_B^0|U^A|\psi_B^0>$ by using the general energy expression (18) but employing one- and two-electron integrals over the operators p^A and q_{12}^A instead of the usual integrals over h and $\frac{1}{r_{12}}$.

We could continue this perturbation treatment by going on to determine second-order and higher corrections. However we will stop here and next consider a self-consistent approach instead.

2. Self-Consistent Treatment

Let us now assume that while U^A is a small perturbation to H it is not small enough to justify a simple first-order perturbation treatment. That is, we will now assume that ψ_B^A can still be taken to be functionally the same as ψ_B^0 but because of the presence of A the spatial orbitals themselves distort away from $\{\phi_i^0\}$ to a meaningful extent. The problem is then to determine these new orbitals $\{\phi_i\}$. Since ψ_B^A is an eigenfunction of electronic motion satisfying (11) this can be done variationally. That is, we can determine these new distorted orbitals by requiring that E_B^A be stationary with respect to changes in these orbitals. If for simplicity (but not necessity) we assume that ψ_B^0 can be written as a Hartree-Fock type wavefunction involving orthonormal

spatial orbitals (or orthonormal spin-orbitals for the case of an
Unrestricted Hartree-Fock wavefunction) then (18) takes on the simple
Roothaan form

$$E_B^0 = 2 \sum_{i=1}^{n} f_i \langle \phi_i^0 | h | \phi_i^0 \rangle + \sum_{i,j} [a_{ij} J_{\phi_i^0 \phi_j^0} + b_{ij} K_{\phi_i^0 \phi_j^0}] \tag{20a}$$

where

$$J_{\phi_i^0 \phi_j^0} = \langle \phi_i^0 | J_{\phi_j^0} | \phi_i^0 \rangle = \langle \phi_j^0 | J_{\phi_i^0} | \phi_j^0 \rangle = \langle \phi_i^0 \phi_j^0 | \frac{1}{r_{12}} | \phi_i^0 \phi_j^0 \rangle \tag{20b}$$

$$K_{\phi_i^0 \phi_j^0} = \langle \phi_i^0 | K_{\phi_j} | \phi_i \rangle = \langle \phi_j | K_{\phi_i} | \phi_j^0 \rangle = \langle \phi_i^0 \phi_j^0 | \frac{1}{r_{12}} | \phi_j^0 \phi_i^0 \rangle \tag{20c}$$

and where $\{f_i; a_{ij}; b_{ij}\}$ are fixed coefficients (for the case of a multi-
configurational wavefunction these coefficients are simply related to the
variationally determined configurational coefficients) which depend on
the precise form of ψ_B^0. Since ψ_B^A is being taken to have the same
form as ψ_B^0 and because of the similarities between H and U^A mentioned
above, we can immediately write our equation for E_B^A as

$$E_B^A = 2 \sum_{i=1}^{n} f_i \langle \phi_i | h^A | \phi_i \rangle + \sum_{i,j} [a_{ij} \langle \phi_i \phi_j | g_{12}^A | \phi_i \phi_j \rangle + b_{ij} \langle \phi_i \phi_j | g_{12}^A | \phi_j \phi_i \rangle] \tag{21a}$$

where the operator h^A and g_{12}^A are given by

$$h^A = h + p^A \ ; \ g_{12}^A = \frac{1}{r_{12}} + q_{12}^A \tag{21b}$$

Therefore, $\{\Phi_i\}$ and therefore E_B^A can be determined using standard

basis set expansion (LCAO) SCF techniques. The only difference is that

instead of using the usual one- and two-electron integrals we must use

integrals over the operators h^A and g_{12}^A instead. However, since

these integrals serve only as imput this difference is transparent to

whatever available SCF procedure we employ.

3. Configuration Interaction Treatment

For the sake of completeness it should be mentioned that since

ψ_B^A can be variationally determined there is no need to stop at the SCF

level and we could solve for this function as a Configuration Interaction

(CI) problem. The only difference form a standard CI calculation is

that instead of using the usual one- and two-electron integrals we must

use integrals over the h^A and g_{12}^A operators defined in (21b). It

should be pointed out however that any solution for ψ_B^A which differs

significantly from ψ_B^0 implies that for that solution U^A can no longer

be regarded as a small perturbation to H and in such a case the validity

of the approximations made in our choice of U^A would become subject

to question. This of course also applies in our SCF treatment as well.

D. The Potentials

The one- and two-particle effective potentials Σ^A and W^A

appearing in our final equations in section II are hermitian adiabatic

approximates to the true field theoretic potentials. As we have mentioned,

such potentials can be obtained in closed <u>ab initio</u> form using many-body theory within the framework of the RPA approximation and taking the adiabatic limits. However, while these potentials are tractable they are nonetheless quite complicated and their use would entail considerable computational effort. In view of the perturbative nature of our theory it is reasonable to expect that we could use potentials having simpler forms. Such simpler potentials can be obtained by making moment expansions of the RPA potentials and truncating these expansions in a physically meaningful manner [5]. When this is done, the resulting potentials can be cast in forms which are very similar to phenomenologically derived semiempirical potentials which have been used by other workers with considerable success [6]. Therefore, it would seem that the use of complicated <u>ab initio</u> potentials is not warranted (although we do reserve the option to do so) and that we can take our potentials to have semi-empirical forms similar to those used by Delgarno and by Victor [6], namely

$$
\int dr' \; \Sigma^A(r;r') \;=\; -\frac{Z^A}{|r|} + \int dr' \; \Sigma^A_{HF}(r;r') - \frac{\alpha^A_d}{2|r|^4} W_6(k|r|)
$$
$$
- \frac{\alpha^A_q}{2|r|^6} W_8(k|r|) + (a_0 + a_1 |r| + a_2|r|^2)e^{-k|r|}
$$

$$(22a)$$

and

$$(22b)$$

$$
\int dr'_1 \; dr'_2 \; W^A(r_1,r_2;r'_1,r'_2) \;=\; -\frac{\alpha^A_d}{|r_1|^2|r_2|^2} W_3(k|r_1|)W_3(k|r_2|)P_1(\cos \gamma_{12})
$$
$$
- \frac{\alpha^A_q}{|r_1|^3|r_2|^3} W_4(k|r_1|)W_4(k|r_2|)P_2(\cos \gamma_{12})
$$

where we have chosen our coordinate system to be centered on A which for simplicity we now take to be an atom having a nuclear charge of z^A
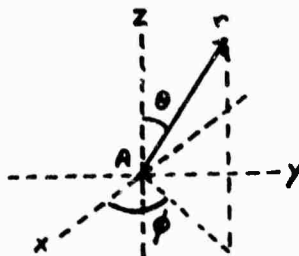
and where

$$W_n(x) = (1-e^{-x^n}) \text{ is a cutoff function}$$

γ_{12} = angle between vectors r_1 and r_2

$P_\ell(x)$ = legendre polynomial of the ℓth degree

α_d^A = dipole polarizability of A

α_q^A = approximate quadrupole polarizability of A (adjustable)

k = approximately $1/2\ r_0$ where r_0 is the effective radius of A (adjustable)

$\{a_i\}$ = adjustable monopole parameters

and

$$\Sigma_{HF}^A (r;r') = \sum_{i=1}^{n_A} \frac{\phi_i^{A*}(r')[2-P_{r,r'}]\ \phi_i^A(r')}{|r-r'|}$$

is the static Hartree-Fock potential of A with $\{\phi_i^A\}$ being the n_A spatial Hartree-Fock orbitals for the electrons in A . $P_{r,r'}$ is the permutation operator if r is an electronic coordinate whereas $P_{r,r'} = 0$

if r is a nuclear coordinate. Note that all quantities are now purely
spatial and that Σ^A and W^A are therefore explicitly spin independent.

In (22a) the first term is simply the potential due to the nucleus
of A and the second term is the static Hartree-Fock potential for the
electrons in A occupying the spatial orbitals $\{\phi_i^A\}$. The next two
terms in (22a) are asymptotically correct induced d pole and quadrupole
polarization potentials which die off rapidly at short distances from A .
The final term is an induced monopole term which serves as a short range
correction potential. The terms in (22b) describe an asymptotically
corre t dielectric potential which properly cancels out one-particle
induced dipole and quadrupole polarizations of A due to two particles
of the same charge when these particles are on opposite sides of A .
That these potentials represent a significant simplif ation over the
ab initio potentials is clear in that our two-particle potential is
strictly local and the only nonlocal term in tne one-particle potential
is simply the usual Hartree-Fock exchange potential. However, despite
their simplicity, potentials such as these have been used very success-
fully for a variety of problems in the past and should therefore be quite
adequate for our purposes.

As it stands, (22b) is concise and to the point. However, one
important property is obscured. This is that our two-particle potential
can be written in terms of one-particle operators only. To see this
we need only express the angle γ_{12} in terms of the spherical angles

for each vector. Thus, by making use of the expansion

$$P_\ell(\cos \gamma_{12}) = P_\ell(\cos \theta_1)P_\ell(\cos \theta_2) + 2 \sum_{m=1}^{\ell} \frac{(\ell-m)!}{(\ell+m)!} P_\ell^m (\cos \theta_1)P_\ell^m(\cos \theta_2)$$

$$[\cos m\phi_1 \cos m\phi_2 + \sin m\phi_1 \sin m\phi_2] \tag{24}$$

where $P_\ell^m(\chi)$ is an associated Legendre polynomial, we find that (22b) can be rewritten as

$$\int dr_1' \ dr_2' \ W^A(r_1,r_2;r_1',r_2') = - \sum_{i=1}^{8} Q_i(r_1)Q_i(r_2) \tag{25a}$$

where

$$Q_1(r) = \sqrt{\alpha_d^A} \ |r|^{-2} W_3(k|r|)P_1(\cos \theta)$$

$$Q_2(r) = \sqrt{\alpha_d^A} \ |r|^{-2} W_3(k|r|) \ P_1^1(\cos \theta) \cos \phi$$

$$Q_3(r) = \sqrt{\alpha_d^A} \ |r|^{-2} W_3(k|r|) \ P_1^1(\cos \theta) \sin \phi$$

$$Q_4(r) = \sqrt{\alpha_q^A} \ |r|^{-3} W_4(k|r|) \ P_2(\cos \theta) \tag{25b}$$

$$Q_5(r) = 1/3 \sqrt{\alpha_q^A} \ |r|^{-3} W_4(k|r|) \ P_2^1(\cos \theta) \cos \phi$$

$$Q_6(r) = 1/3 \sqrt{\alpha_q^A} \ |r|^{-3} W_r(k|r|) \ P_2^1(\cos \theta) \sin \phi$$

$$Q_7(r) = 1/12 \sqrt{\alpha_q^A} \ |r|^{-3} W_4(k|r|) \ P_2^2(\cos \theta) \cos 2\phi$$

$$Q_8(r) = 1/12 \sqrt{\alpha_q^A} \ |r|^{-3} W_4(k|r|) \ P_2^2(\cos \theta) \sin 2\phi$$

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